PETROLEUM AND NATURAL GAS RESEARCH PROGRAM BUREAU OF MINES, FISCAL YEAR 1952

BY R. A. CATTELL AND OTHERS

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by

R. A. Catteil[1] and others

CONTENTS

	Page
Summary and introduction	1
Acknowledgments	5
Oil and gas development and production	6
Petroleum-engineering studies	6
Scurry Reef reservoir, Scurry County, Tex.	6
Chemical characteristics of waters from Canyon, Strawn, and Wolfcamp formations in Scurry, Kent, Borden, and Howard Counties, Tex.	7
Big Lake field, Tex.	7
Pressure build-up and well-interference tests, Scurry County, Tex	7
Study of reservoir-oil samples	8
Variations in composition of Scurry Reef reservoir oil, Scurry County, Tex.	8
Variation in composition of reservoir oil in Rangely field, Colo.	8
Study of Basal Sundance reservoir, Lance Creek field, Wyo.	9
Evaporation of reservoir oil by cycling gas	9
Characteristics of gas-condensate fluids	10
Well-spacing studies	12
Drilling-fluid research	13
Quebracho substitutes	14
Equipment for sampling and analyzing fluids from deep wells	14
Sulfur recovery	14
Helium-tracer studies	14
Secondary recovery	15
Field studies	15
Survey of secondary-recovery operations in California.	15
Survey of water flooding in Oklahoma	16
Survey of water flooding in northeastern Kansas	16
Nowata County, Okla.	16
Healdton field, Okla.	17
Quapaw field, Okla.	17
Flat Rock field, Okla.	18
Southwestern part of K.M.A. field, Tex.	18
North and West Central Texas	19
Cabin Creek field, W. Va.	19

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CONTENTS (Cont.)

	Page
Secondary recovery (Cont.)	
Special field problems	20
Finding of abandoned wells	20
Subsurface measurements to determine physical properties of petroleum reservoirs (selective plugging)	20
Selective plugging of air-gas injection wells	21
Conditioning water for subsurface injection	21
Resistivity of formation waters in north Texas	22
Water-flooding studies	22
Flowing of oil wells on gas-injection projects	23
Shooting oil and gas wells with explosives	24
Laboratory studies	25
Core and water laboratories	25
Effect of brine solutions on permeability	25
Recovery efficiency of water-flooding high-viscosity oils	26
Correlation of residual saturation, after laboratory air-drive tests, with pore patterns of sandstones	26
Gravitational drainage of oil from unconsolidated sands	27
Corrosion of metals by dissolved gases in water	27
Tracers in waters used for subsurface injection	28
Electrical analogy flow studies of gas injection and water flooding	29
Electrical logging	29
Retention of petroleum by reservoir rock	30
Fluid-flow phenomena	30
Detergents in water-flooding operations	30
Reservoir materials	31
Surface-active and film-forming constituents of petroleum	31
Recovery of hydrocarbons from bituminous sandstones	31
Petroleum chemistry and refining	32
Characteristics and availability of crude oils and products	32
Sulfur compounds in petroleum	33
Synthesis, purification, and determination of properties of sulfur compounds	34
Separation and identification	35
Thermal decomposition of sulfur compounds	37
Chemical studies of fuels	37
Gasoline	37
Diesel fuel	37
Nitrogen compounds in distillate fuels	39
Combustion research on fuels	40
Constant-volume bomb	40
Engine studies	41
Fuel surveys	41
Composition of petroleum asphalt	41
Thermodynamics of petroleum	42
Low-temperature calorimetry	43
Vapor-heat capacity and heat of vaporization	44
Combustion calorimetry	44
Vapor-liquid equilibria	45
Statistical mechanical calculations	45

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Page

Transportation of natural gas..... 45
Removal of excess nitrogen from natural gas..... 45
Dew-point recorder for natural gas..... 46
Flow of natural gas in pipelines..... 46

TABLES

1. Indicated precision of phase diagram computation methods.. 11
2. Indicated precision of compressibility computation methods 12
3. Sulfur compounds identified in Wasson, Tex., crude oil and estimated weight percent present where known..... 35

ILLUSTRATIONS

Fig. Follows page

1. Water-flood operators and engineers at project during tour of water-flood plants in Nowata County, Okla. .. 16
2. Production history of Nowata County, Okla. 16
3. Comparison of actual reservoir performance utilizing pressure maintenance and calculated theoretical reservoir performance without pressure maintenance, K.M.A. reservoir, southwestern part of K.M.A. field, Wichita and Archer Counties, Tex. 18
4. Calculated theoretical production history of one 20-acre, five-spot water-flood project, zone 1, K.M.A. reservoir, southwestern part of K.M.A. field, Wichita and Archer Counties, Tex. 18
5. Water-input profile..... 20
6. Apparatus to measure bulk volume of core samples..... 24
7. Composite photograph of laboratory dissolved-gas corrosion apparatus..... 28
8. Laboratory water-tracer adsorption apparatus, showing test in progress..... 28
9. Physical-properties laboratory, showing refractometer in foreground and density determination being made on specific-gravity balance..... 28
10. Systematic separation of sulfur compounds..... 34
11. Sulfur-stability test of selected crude oil..... 36
12. Thermal decomposition products from sulfur compounds are analyzed by means of the mass spectrometer..... 36
13. Apparatus for catalytic decomposition of thiacyclopentane..... 36
14. Observed and calculated pressure records - fuel injected into inert gases (using constant-volume combustion bomb)..... 40
15. Rotating bomb and its constant-temperature container used for studies of the heats of combustion of corrosive sulfur compounds..... 44

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SUMMARY AND INTRODUCTION

The conditions under which the researches of the Bureau of Mines on petroleum and natural gas were conducted in 1952 were little changed from those indicated in the last report,2/ which dealt with activities during 1951, immediately after crossing of the 38th Parallel by the North Korean Army. Although only a small part of the program was classified in the military sense, there was a feeling of the clash of world forces which called for even closer scrutiny of the research problems so that the emphasis could be placed without delay where the greatest needs for national defense seemed to be. The reports of the work accomplished were so directed as to have the greatest immediate value to persons charged with supply planning for the military forces and included information on the availability and characteristics of a wide variety of crude oils, fuels, and other petroleum products.

Actually, the approach, direction, and conduct of the work do not differ greatly under the two circumstances, as has been pointed out in earlier reports; only the tempo changes.

One thing is clear; to maintain a backlog of scientific information as a very important national resource to be drawn upon as needed in peace or war, advances must be made continually in petroleum technology as well as the other sciences by accumulating new and fundamental knowledge. If the steady increase in this store of knowledge is interrupted, progress will falter, and to maintain this high level the costs of research must be met. Not only is instrumentation costly, but the dearth of trained scientific personnel has created a seller's market. All things considered, scientific knowledge is bought more dearly as the borders of research are extended far beyond the conventional thinking of a few short years ago.

Despite the condition of the technical labor market, making it difficult to obtain well-trained engineers and scientists, a comprehensive study of reservoir conditions in the Scurry Reef reservoir in Texas, as a cooperative undertaking by the Bureau of Mines and the Geological Survey, United States Department of the Interior, was completed ahead of schedule to the expressed satisfaction of the oil operators in the field and the Petroleum Administration for Defense. The first study, which was completed only 6 months after the work was begun, dealt with pressure build-up and well-interference tests in the Kelly-Snyder area where gas injection as a stimulative method was contemplated. The derived information was revealing, as it pertained to the effective permeability of the rocks comprising that part of the reservoir and the suitability of the reservoir for application of pressure maintenance. There followed in rapid succession an analysis dealing with a survey of the gravity of the oil produced under controlled conditions in the reef formation, a second study on pressure build-up and interference tests on wells extending the initial study to other carefully selected wells throughout the field, variations in the content of solution gas in the Scurry Reef reservoir oil, a summary of the

2/ Cattell, R. A., and others, Petroleum and Natural-Gas Research Program, Bureau of Mines, Fiscal Year 1951: Bureau of Mines Inf. Circ. 7643, 1952, 46 pp.

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chemical characteristics of the waters from various formations in Scurry and adjacent counties, and finally, near the close of the year, an engineering study of the Scurry Reef reservoir. An appraisal of the value of this work to those directly concerned with getting oil out of the reservoir to meet the Nation's needs has been given by the chairman of the Engineering Committee of the Scurry Area Canyon Reef Operators Committee in a letter addressed to the Deputy Administrator for the Petroleum Administration for Defense. The Chairman stated in part:

> For some time we have been enjoying the benefits of the work performed by the U. S. Bureau of Mines in the Scurry Reef fields, and I would like to have you know that the operators, and particularly the Engineering Committee of the Scurry Area Canyon Reef Operators Committee, believe that the Bureau's work is proving to be of material assistance. The operators have agreed that unitization is required to obtain maximum conservation and maximum production.
>
> * * * *
>
> The decision of the operators to form the Unit was made upon the recommendations of their engineers. The U. S. Bureau of Mines has been of material assistance in developing the facts upon which these recommendations have been based. Over the years the research and investigations of the Bureau of Mines have strengthened greatly the background for conservation of petroleum, and specifically in the Scurry Reef, recent studies made by the Bureau are especially important.

The full value of this work will not be known until long after the area is unitized. However, no one can dispute the fact that the recoverable reserves of petroleum in the Scurry Reef fields have been increased materially because of the application of sound engineering methods of operation based upon the teamwork study of industry and engineers of the Bureau of Mines. Bureau of Mines engineers have the advantage of viewing the problem objectively without regard to property lines and without the bias that is likely to enter into decisions involving correlative rights. The experience gained in the reef area will be of inestimable value in a teamwork approach to other large oil-producing areas, such as the Spraberry fields of West Texas, which present many intriguing problems of oil availability.

Interest of the petroleum industry continues to grow in methods whereby reserves may be increased through stimulative methods. The search is being extended in ever widening circles for areas that are suitable to water-flooding operations. A real contribution to the literature of oil production is a survey report on water-flooding projects in Oklahoma, published in two volumes. These references have been considered so valuable by persons giving close study to the subject that a sizable part of the historical information contained in the report was incorporated into a summary of secondary-recovery operations in Oklahoma to 1951, which was published recently as a joint survey by the State of Oklahoma and the Interstate Oil Compact Commission.

A survey of current fluid-injection projects in California was published. This is the first Bureau report on secondary-recovery projects in California and includes pressure maintenance by both water and gas injection, gas drive, and water flooding. It describes and evaluates typical projects in 15 fields of the State.

In addition, reports on selected fields in which detailed studies were made have shown what may be accomplished and have suggested general areas in which oil operators should be able to apply these methods with reasonable assurance that their

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reserves of petroleum will be augmented if stimulative methods are applied. Typical of the reports of this type are those on the Healdton field of southern Oklahoma and the K.M.A. field of North Texas. Also an engineering study of gas-injection operations in a part of the Cabin Creek field, W. Va., was published.

Another major activity of the group studying secondary-recovery methods is described in a series of reports on water treating, which has set guidelines for proper handling and treatment in all oil-producing areas where water is an adjunct to oil production or has become a problem of disposal.

A few years ago the Bureau began pioneer work in surface chemistry as applied to the relationships of reservoir fluids and reservoir rocks. At that time, some persons felt that this was a highly theoretical approach to the very practical subject of oil production and might lie beyond the boundaries of the field that petroleum engineers should cover. Actually, the work is physical chemistry; to that end, qualified physical chemists were employed for the task. Today hardly an oil company conducting research is not giving particular attention to some of the highly theoretical aspects of surface chemistry as it relates to the behavior of petroleum in contact with the reservoir rocks.

One problem that has created much interest deals with electrokinetics. Many persons would associate electrical energy with oil production only insofar as that energy is brought into an oil field with wires or other transmitting equipment. Actually, minute electrical forces (potentials) generated by the flow of fluids through the porous rocks of the reservoir may have certain effects upon oil recovery. The study of electrokinetics contributes to the understanding of these phenomena. The research that Bureau investigators have conducted on "streaming potentials" should yield useful information in ascertaining the magnitude of these electrical forces and, if they affect oil production, whether they can and should be minimized to increase the efficiency of production.

Naturally, work in the surface-chemistry laboratories directs attention to the peculiar qualities of detergents, popularly and perhaps incorrectly referred to as soapless soaps. In its studies of the use and effects of these agents, the Bureau is following its long-established practice of meticulously avoiding borderline problems that involve proprietary rights.

Advancing the study of Diesel fuels, sponsored and supported by the Western Petroleum Refiners Association, the tests on the instability and incompatibility of Diesel fuels in storage reached a point where certain patterns of behavior, with reasons therefor, began to take definite shape. Because of the widespread scope of these tests (3,000 samples stored under different conditions), which are yielding a large quantity of data on a number of representative fuels, it appears evident that previous investigations based upon a study of one fuel or on one type of fuel have resulted in misleading conclusions that may not be applicable to other types of fuels.

The constant-volume combustion bomb, in which small quantities of fuel are burned to determine the manner in which ignition and combustion characteristics are related to the composition of the fuel, has passed the development stage. The bomb is being used to obtain reproducible data not only on selected petroleum fractions of high purity but on commercial-type Diesel fuels as well. These results are attracting widespread interest from the Navy, other large users of Diesel fuels, and the manufacturers of Diesel engines and have resulted in cooperative projects with the Coordinating Research Council and the Navy for special tests using this instrument. Again, representatives from these groups and others came to Bartlesville from various parts of the country to hear reports on the Diesel-fuel program and participate in the discussions. A very informative panel discussion was featured, conducted

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by outstanding representatives in industry who are authorities on the performance and availability of Diesel fuels.

American Petroleum Institute Project 48A, conducted at Laramie, Wyo., and Bartlesville, Okla., showed marked progress in its three divisions: (1) Synthesis, purification, and determination of properties of sulfur compounds; (2) separation, isolation, and identification of sulfur compounds in crude oil; and (3) determination of thermodynamic data of sulfur compounds. A high point of the year's work was definitely establishing that elemental sulfur occurs in some crude oils, a subject that has been highly controversial for years. The full significance of this find in the research field of sulfur compounds in crude oil is only conjectured. Assuredly, if refiners know that a certain crude oil contains elemental sulfur, they are in a position to take steps to refine it more expeditiously and effectively with this knowledge than if their treatments for sulfur removal were not predicated on this basic knowledge. The number and scope of reports both for publication and to the sponsoring agency in the form of progress reports on Project 48A attest the completeness with which this problem of basic interest to the petroleum and petrochemical industries is being investigated.

That part of the project dealing with the determination of thermodynamic data of sulfur compounds also is attracting wide attention. The rotating bomb for determining the heats of combustion of various sulfur compounds has passed the development stage and now is being used to obtain a large fund of thermodynamic data as background information for plant design and construction. This particular research tool is the first of its kind and has attracted international notice. The International Union of Thermochemistry has asked members of the Bureau of Mines Thermodynamics Laboratory at Bartlesville to prepare two chapters dealing with application of this bomb to the combustion of sulfur and chloro compounds, which will be included in a book being prepared on Experimental Thermochemistry. Also, the Bureau has been fortunate in having three separate visits from professors from the University of Lund, Sweden. Each visitor has spent considerable time in the Bureau laboratories collaborating on work being conducted only in laboratories of the University of Lund and the Bureau of Mines. For the first time a broad, systematic attack on this part of the sulfur problem has been developed, and an accurate picture of the thermodynamic properties of several families of sulfur compounds is being developed. The same careful and painstaking approach is manifest in the other thermodynamic researches discussed in the body of this report.

Foreign nationals by no means were restricted to representatives of Sweden. A petroleum engineer on a training grant, who was sent by the Brazilian Government, is spending a full year at the Bartlesville Station. Through the Institute of International Education, a chemist of the Fuels Experiment Station, Milan, Italy, is working on the decomposition of sulfur compounds as a University of Wyoming fellow at the Bureau of Mines Laramie Station. In addition to those assigned for periods varying from a few weeks to a full year, there has been a wide variety of casual visitors, and the list of 13 nations given in the report for last year has been increased by visits from engineers from Brazil, India, Chile, and Israel, as well as by many new visitors from the earlier-mentioned countries.

As a stimulus to good-will relations with other nations, the services of a Bureau of Mines engineer, who has an international reputation in secondary-recovery and pressure-maintenance technology, were made available to the United Nations. He was sent to Yugoslavia on a special assignment to aid the engineers of that country in coping with some of their oil-production problems. In addition, a petroleum chemist and a petroleum engineer of the Bureau of Mines attended the Third World Petroleum Congress at Leiden, Netherlands, and presented papers on the composition

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of crude oils and stimulative methods of oil production. Thus are the ends of technical understanding and attending human relations advanced.

In spite of a variety of situations of uncertainty and the high cost of conducting the types of work in which it is engaged, the petroleum and natural-gas studies of the Bureau of Mines during the past 12 months have satisfactorily discharged the responsibility of keeping a steady stream of new and accurate data concerning fundamental and practical research flowing from laboratories and field assignments to industry, Government, scientific groups, and the public.

The specific accomplishments are described briefly in the following sections under the same general captions used in earlier reports, namely: Oil and Gas Development and Production; Secondary Recovery; Petroleum Chemistry and Refining; Thermodynamics of Petroleum; and Transportation of Natural Gas.

ACKNOWLEDGMENTS

This annual report of the Bureau's petroleum- and natural-gas-research activities was prepared from reports submitted by the scientific staffs in five field headquarters in four of the Bureau's nine regions and by the staff of the Director's office in Washington. Acknowledgment is made to the following regional directors and their staffs for their valuable assistance:

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Many research projects described in this report were given great assistance through the excellent cooperation and generous help of the petroleum and natural gas industry. Grateful acknowledgment is made for this assistance. Furthermore, substantial assistance was given to parts of the research programs through 18 cooperative agreements, which resulted directly in increased accomplishments. For this the Bureau of Mines makes grateful acknowledgment and expresses appreciation to the following cooperators: State of Oklahoma, Kansas State Board of Health, Arkansas Oil and Gas Commission, University of Wyoming, Texas Technological College, American Gas Association, American Petroleum Institute, American Society for Testing Materials, Coordinating Research Council, Inc., North Texas Oil and Gas Association, Pennsylvania Grade Crude Oil Association, Western Petroleum Refiners Association, and the Ethyl Corp.

OIL AND GAS DEVELOPMENT AND PRODUCTION

Petroleum-Engineering Studies

Scurry Reef Reservoir, Scurry County, Tex.

Through an agreement between the Bureau of Mines, the Geological Survey, and the Petroleum Administration for Defense, Bureau of Mines engineers have completed a comprehensive study of the Scurry Reef reservoir in Scurry and adjacent counties in Texas. This study was made to furnish the Petroleum Administration for Defense with engineering data and other information that would aid the Administration in meeting its responsibilities under the Defense Production Act. Approximately 1,625 wells are producing from this reservoir, which underlies an area of about 64,000 acres.

The Scurry Reef reservoir is comprised of two fields (Diamond M and Kelly-Snyder as designated by Texas Railroad Commission), which were discovered individually, but subsequent development proved that they are part of one continuous reservoir. The discovery well of this reservoir was the Standard Oil Co. of Texas, Jessie Brown well 2-1 completed November 19, 1948. Development of the two fields was slow during the first year, and only 237 wells were completed by November 1949. Drilling activity increased as the two areas merged, and by the end of November 1951, 3 years from discovery date, 1,617 producing wells had been drilled.

The reservoir is one of the largest in the United States, and the reserves in it will be important contributors in fulfilling any accelerated requirements of the defense program. Accordingly, the Bureau of Mines undertook a comprehensive study of the reservoir. Data were collected from the analyses of samples of cores from 72 wells and from quantitative interpretations of approximately 1,400 electric logs and 400 radioactivity logs. Core analyses were made on both large-diameter cores and conventional plugs. Porosity data from the logs were compared with core analyses, and correction factors were derived by which log porosities were converted to the equivalent of porosities from core analyses. Interstitial water was determined by both the evaporative and the restored-state methods. Determinations were made on 1,567 core samples from 66 wells.

The characteristics of the reef varied widely, and all reservoir data were averaged volumetrically in an endeavor to derive true averages. To accomplish this a method not previously used by petroleum technologists for volumetrically weighting reservoir data was developed. A description of this method, involving use of polygonal prisms, has been published.3/

3/ Anderson, K. F., A Rapid Method for Volumetrically Weighting Reservoir Data: Oil and Gas Jour., vol. 51, No. 3, May 26, 1952, pp. 202-205.

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Chemical Characteristics of Waters from the Canyon, Strawn, and Wolfcamp Formations in Scurry, Kent, Borden, and Howard Counties, Tex. - Information relative to the oil-field brines from the Scurry Reef formations in Scurry and adjacent counties was derived from water analyses obtained from cooperating companies and from Bureau of Mines analyses. The results of water analyses were tabulated and indexed, chemical characteristics of the different formation waters were determined, and ionic ratios were calculated and tabulated. Graphical illustrations and contour maps were used to compare characteristics of the different waters. Pertinent information on the manner of well completion and the method of obtaining the water samples was included in tables so that the characteristics could be evaluated correctly. The need for information pertaining to the chemical characteristics of formation waters from the Scurry County area has increased because of contemplated pressure-maintenance programs and increased rates of water production. The chemical compatibility of injected water with the interstitial water in a reservoir must be determined to prevent deposition of salts that might plug capillaries, thereby decreasing the permeability of the formation. Information derived from studies of water analyses is used in solving many problems involving formation correlation, detection of well leaks, drill-stem testing, and identification of water sources.

Big Lake Field, Tex.

Writing of the final report giving a petroleum-engineering analysis of the Ellenburger reservoir in the Big Lake field, Reagan County, Tex., was reactivated near the end of the fiscal year. The work was suspended a year ago owing to necessary assignment of the personnel engaged in the study to the Scurry Reef reservoir project, discussed before.

Pressure Build-Up and Well-Interference Tests, Scurry County, Tex.

The results of field tests on wells at seven different locations in the Scurry Reef oil field of West Texas were used to develop information on the physical characteristics of the reef reservoir rock and on fluid movement in the reservoir as the oil is being produced. The conclusions in the report, first submitted on a restricted basis to the Petroleum Administration for Defense and later published,4/ were that reservoir conditions within the areas tested favored maintenance of pressure by injecting gas or water to increase the recovery of oil. The criteria to be satisfied in planning application of pressure maintenance as a producing procedure are that the producing formation is permeable enough to permit injection of practical volumes of fluid, that the oil reservoir is interconnected, and that the formation is free of highly permeable channels between wells.

The pressure build-up and interference tests showed that: (1) The effective permeability of the drainage areas of the wells tested ranged from 4.6 to 36 millidarcys; (2) no highly permeable channels existed between the test wells and offset wells, as indicated by the slow, continuous pressure increases over periods ranging from 39 to 120 hours; (3) the reservoir within six of the areas tested was interconnected, as indicated by pressure decreases near the end of the test period - the tests on one well gave no positive indication of interconnection after being continued for 7 days; (4) the methods used to complete the wells were adequate because the over-all permeability of the entire drainage area was greater than the effective permeability of the reservoir rock, indicating that the formation in the immediate vicinity of the well bore had not been reduced in permeability by the well-completion method used.

4/ Smith, R. V., Williams, R. H., Dewees, E. J., and Archer, F. G., Well-Interference and Pressure Build-Up Tests. Part I: Oil and Gas Jour., vol. 51, No. 14, Aug. 11, 1952, pp. 118-125. Part II: Oil and Gas Jour., vol. 51, No. 15, Aug. 18, 1952, pp. 99-105, 124-127.

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Study of Reservoir-Oil Samples

Variations in Composition of the Scurry Reef Reservoir Oil, Scurry County, Tex.

A new method was used to determine the extent of variations in physical properties of the reef reservoir oil in Scurry County, Tex. Because of the magnitude of the reef reservoir in Scurry County, the normal procedure of obtaining and analyzing reservoir oil samples from about one well in each section of land would have been impractical. Because the reservoir oil was not saturated with gas initially, the production gas-oil ratio from a well would represent the solution-gas content of the oil from that part of the reservoir. Gas-oil-ratio well tests were made on 45 wells producing from the Scurry County Reef and subsurface oil samples were obtained from 7 of these wells. These subsurface oil samples have been analyzed to obtain knowledge of the physical properties that are desirable for calculating the availability and reserves of oil and in predicting the feasibility of the application of pressure maintenance. The physical properties of the oil samples from the seven wells were compared with the solution (production) gas-oil ratios from these wells and reliable correlations of solution gas-oil ratios with the other physical properties of the subsurface- (reservoir) oil samples determined in the laboratory were established. Thus, the physical properties of the reservoir oil can be determined for other parts of the field by comparing the production (solution) gas-oil ratios for the 38 wells tested and not sampled (45 minus 7) with the above-mentioned correlations.

A study of the production gas-oil-ratio data and the data obtained in the laboratory on the subsurface-oil samples led to the conclusion that the oil in the southwestern part of the reservoir at 4,300 feet subsea contained 135 cubic feet per barrel more solution gas than the oil in the northeastern part of the reservoir at the same depth. Moreover, it was concluded that the reservoir oil varied in composition with depth, there being a decrease in solution-gas content of the oil of 46 cubic feet per barrel for each 100 feet increase in depth.

Variation in Composition of Reservoir Oil in Rangely Field, Colo.

Engineering studies of oil and gas fields in the Rocky Mountain area received primary emphasis. A report of a study of the Rangely oil field, Colo., was published in April 1951.5/ A condensed version of this report appeared late in 1951 6/ and brought additional attention to the findings of unusual varying oil characteristics in the Weber sandstone reservoir. A study was made of the possible effects of the high nitrogen content of the solution gas and the variation with pressure of the composition of liberated gas on the heating value of future produced gas. It was determined that, during the producing life of the field and as production gas-oil ratios increase, the net heating value of produced gas should decrease and might range between 800 and 900 B.t.u. per cu. ft. The net heating value of the original solution gas averaged 1,139 B.t.u. per cu. ft. Knowledge of this condition was particularly important in making an engineering study of this gas reserve as a possible source of fuel.

5/ Cupps, C. Q., Lipstate, P. H., Jr., and Fry, Joseph, Variance in Characteristics of the Oil in the Weber Sandstone Reservoir, Rangely Field, Colo.: Bureau of Mines Rept. of Investigations 4761, 1951, 68 pp.

6/ Cupps, C. Q., Lipstate, P. H., Jr., and Fry, Joseph, Variation of Oil Characteristics with Elevation in Oil Reservoirs: World Oil, vol. 133, No. 7, December 1951, p. 192.

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Study of Basal Sundance Reservoir, Lance Creek Field, Wyo.

A long-range study, begun in 1937, of underground conditions and reservoir performance of the Basal Sundance reservoir, Lance Creek field, Wyo., was nearly completed. This reservoir was discovered early in 1935, and a unitized pressure-maintenance program of gas injection has been in effect since early 1938. Observations of the reservoir-oil characteristics have been made periodically, using subsurface oil samples obtained from key wells. Several interesting facts have been disclosed. The drying action of the injected gas has caused loss of some components of the reservoir oil with which this gas has come in contact and has changed the oil characteristics. In a relatively isolated part of the reservoir, an opposite effect has been observed where surplus propane and butane had been injected. There also are definite indications that the laboratory technique of differential liberation of a reservoir oil yields data corresponding to the process of liberation of gas in the reservoir with pressure decline. As indicated by the study, this pressure-maintenance program may result in an additional recovery of 8 to 11 percent of the initial oil in place.

Evaporation of Reservoir Oil by Cycling Gas

That part of the science of reservoir engineering dealing with calculation of the benefits of increased oil recoveries to be derived by pressure maintenance is relatively new. Material-balance equations are used along with P-V-T data on the reservoir oil and gas and relative permeability data of the flow of gas and oil in the reservoir rock. This method appears to be sound fundamentally; however, there is need for improvements and refinements of the method. A report7/ was published in 1951 showing the importance of taking into consideration the liquefied-petroleum products that will be derived from the production of the solution gas that is liberated in a reservoir containing a highly volatile oil and being produced by the solution gas-drive mechanism.

A study has been begun to point out another refinement in making reservoir engineering calculations. In planning a pressure-maintenance program of cycling gas the operators consider three possible benefits: (1) Increased oil recovery; (2) prolonged flowing life of the wells resulting in reduced lifting costs; and (3) a gas reserve that will be available after oil production ceases. When gas is first passed through a reservoir it propels oil to the producing wells. However, oil is not flushed out completely from the pore space in the reservoir rock, but additional oil is carried to the producing wells as gas continues to be cycled through the reservoir. The amount of oil produced each time the gas is cycled through the reservoir becomes less until the oil saturation in the pores of the reservoir rock becomes so low that the oil is virtually immobile. Nevertheless, 20 to 50 percent of the oil may remain in the reservoir at this time. After the gas reaches a producing well, along with the oil, the natural-gasoline components are recovered in a gasoline plant before the dry gas is returned to the reservoir. It is logical to assume that some of the oil evaporates as the dry gas passes through the reservoir and these products of evaporation are recovered in the gasoline plant. No technical paper has been presented to show a method of estimating the recoverable liquefiable products resulting from evaporation as gas is cycled through a reservoir in a pressure-maintenance project.

Equipment has been designed, constructed, and set up in a Bureau of Mines laboratory to determine the rate of evaporation when dry gas is cycled through a

7/ Cook, Alton B., Spencer, G. B., and Bobrowski, F. P., Special Considerations in Predicting Reservoir Performance of Highly Volatile Type Oil Reservoirs: Am. Inst. Min. and Met. Eng., Jour. Petrol. Tech., vol. 3, No. 2, February 1951, pp. 37-46.

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reservoir. The equipment consists of a high-pressure, steel, cylindrical vessel filled with fine-grained sand representing an oil reservoir. The pore space between the sand grains is filled with a known volume of reservoir oil of known composition. Dry gas of known composition is injected through a single valve in one end of the reservoir, and fluid is released through two valves at the other end; the liquid phase is released through a valve in the bottom of the end piece and the gas through a valve in the top of the end piece. Two glass windows, designed and constructed to withstand high pressures, are at opposite sides of the end piece, so that visual inspection permits the operation of these two valves to maintain a level gas-oil interface between the valves. An electric-driven, calibrated mercury pump is placed in the system to furnish mercury of known volumes to displace the dry gas from a storage tank into the reservoir at constant pressure. The rate of injection of mercury is controlled electrically by a contact in a pressure diaphragm where the gas pressure is balanced against weights on a dead-weight tester. The volume and composition of both the gas and oil released from the reservoir is determined by low-temperature fractional analysis equipment. Thus, by knowing the volume and composition of (1) the reservoir oil, (2) the injected gas, (3) the produced oil, and (4) the produced gas, the volume of each hydrocarbon evaporated from the oil by the gas and the volume and composition of the oil remaining in the reservoir are determined.

Preliminary tests of passing dry gas through the laboratory reservoir indicate that the equipment will function properly. Reservoir-oil samples, to be used in the evaporation experiments, have been obtained from the reef reservoir in Scurry County, Tex., and a large quantity of high-pressure dry gas has been put in storage. Samples of this oil and gas have been analyzed. Tests on the Scurry County oil will furnish the operators in the Scurry Reef field with information valuable as a guide to production procedure in applying pressure maintenance through the period that the reservoir is being depleted of oil.

Characteristics of Gas-Condensate Fluids

The manuscript, Phase Relations of Gas-Condensate Fluids now has 485 illustrations and tables ready for a volume expected to contain 580 pages. The sections pertaining to the phase diagram and compressibility characteristics of fluids have required particularly detailed study. Published and unpublished data of the Bureau of Mines and data available in the literature have been correlated so that both characteristics may be determined by processes of computation involving relatively little test procedure. In general, the accuracy obtained by using the computations increases with the amount of test information obtained for their application, and the time required and the costs involved increase in the same order.

The precision of the phase-diagram computation methods, as determined from the experimental data used in the correlations, is given in table 1 with a brief statement of the tests required to apply each method. Method I involves only simple testing in field and laboratory, and the results that will be obtained in applying the correlation are subject to an uncertainty in pressure of 180 lb. per sq. in. and an uncertainty in temperature of 12° F. Methods II, III, and IV, in that order, require increasing expenditure of test time and involve increasing test difficulties, but the uncertainty of the results decreases correspondingly, until for method IV, the uncertainty in pressure and temperature is reduced to 53 lb. per sq. in. and 3.8° F. It is estimated that when all necessary full-scale and mobile test equipment are used to obtain measured values for the complete phase diagram of a gas-condensate fluid (method V), the uncertainty in the results obtained is 20 lb. per sq. in. and 2° F. Comparison of methods I, IV, and V as to the time required for testing and computations indicates that the times are, respectively, in the approximate proportion 1:5:50. The costs of equipment for the respective tests are in the approximate proportion 1:2:20. If the operator does not need the accuracy attainable by using the complete test, one of the phase-diagram computation methods will permit a substantial saving of time and equipment investment cost.

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TABLE 1. - Indicated precision of phase diagram computation methods

Method	Test Requirement	Pressure uncertainty, p.s.i.	Temperature uncertainty, °F.
I	Measure liquid-gas ratio with standard separator in field. Hempel-type distillation analysis. Simple computations.	180	12
II	Measure liquid-gas ratio on total flow stream from well with special high-pressure separator. Simple computations.	170	13
III	Measure liquid-gas ratios over narrow range of pressures at temperatures including 100° F. using standard separator. Hempel-type distillation analysis. Computations less complex than those required in applying method IV.	105	8.3
IV	Measure liquid-gas ratios over narrow range of pressures at temperatures certain to include critical temperature - usually approximately 100° F. Hempel-type and low-temperature distillation analyses. Relatively complex computations.	53	3.8
V	Complete test with all necessary full-scale and mobile equipment.	20	2

Engineering work in the oil and gas fields often requires accurate knowledge of the compressibility of a gas when time or circumstance does not permit measurement of the compressibility with suitable equipment. Two correlations of compressibility have been prepared, which require, in test procedure, only a measurement of specific gravity using a gas balance. Method 1 in table 2 may be applied to a wide variety of natural gases and gas-condensate fluids in all phase states, with an uncertainty averaging 1.40 percent. The 10 percent of the data subject to the highest error residuals indicates an uncertainty of 4.6 percent. An accuracy of 3.0 percent is considered good practice in measuring gas with orifice meters, and estimates of reserves are subject to much greater uncertainty. Less than 1 hour usually is required to measure gas specific gravity with a gas balance and to apply method 1 to determine the compressibility of the gas at any pressure up to 5,000 lb. per sq. in. and any temperature in the range 40° to 280° F. As shown after method 4 in the table, the compressibility of a gas may be measured directly with an accuracy of 0.06 percent, but use of the special laboratory equipment required usually will require a minimum of several hours and approximately an additional hour of time for each pressure-temperature condition of interest.

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TABLE 2. - Indicated precision of compressibility computation methods

Method	Test Requirement	Percentage uncertainty	
		Average datum	10 percent with highest residuals
1, sp. gr. 0.5 to 1.1	Measure specific gravity of natural gas or gas phase of gas-condensate fluid, using gas balance.....	1.40	4.6
2, sp. gr. 0.5 to 1.0	Measure specific gravity of gas containing high concentrations of ethane and propane, using gas balance.....	1.77	6.3
3, Z_m, 0.7 to 1.0; sp. gr., 0.5 to 1.1	Measure minimum value of gas compressibility (Z_m) at 100° F., using simple apparatus.....	1.01	4.0
4	Compressibility measurements with complete P-V-T equipment.....	.06	

Because ethane and propane strongly influence the compressibility of natural gas but do not liquefy at atmospheric pressure and temperature, compressibility computation method 2, requiring a test with a gas balance, was developed for refinery gases that are rich in the heavier hydrocarbons. Compressibility computation method 3 was designed to give the accurate compressibility of a gas irrespective of the molecular weight and liquefaction characteristics of its components. Test procedure involves use of a simplified compressibility equipment at 100° F. and the pressure at which the value of the compressibility factor is minimum. More time is required to determine the minimum-compressibility factor than is required to determine the specific gravity using a gas balance, but the average uncertainty of the computation is reduced to 1.01 percent.

For most industrial applications, the percentage uncertainty of methods 1, 2, and 3 is acceptable, and use of the methods will permit a substantial saving of time when the compressibility at a single pressure and temperature is needed. When the compressibility over a wide range of pressures and temperatures is needed, weeks of time may be saved by using the computation methods because of the time required for all the measurements with P-V-T apparatus.

Well-Spacing Studies

For years Bureau engineers have made empirical analyses of oil-field data to develop generally acceptable well-spacing - oil-recovery relations. This work so far has not disclosed defensible relations. Recognizing the economic importance of the results being sought, however, and knowing what such results would mean with respect to oil and gas conservation, Bureau engineers have subordinated rather than abandoned this approach to the problem.

More recently attention has been given to a comprehensive theoretical study, which has been made to uncover the elements of the problem and to reveal barriers to solution. A manuscript tentatively entitled "Multiphase Flow Theory and the Problem of Spacing Oil Wells" has been prepared and is intended for eventual publication.

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This report was perceived as a means of presenting and discussing the well-spacing problem in its simplest mathematical form and is primarily an exposition of the scientific and engineering principles that would underlie any theoretical solution of the problem. Fluid mechanics applied to the behavior of multiphase fluids (gas-oil-water mixtures) in porous mediums (oil-reservoir rocks) represents the main technical basis for the undertaking.

The paper includes a discussion of the well-spacing problem in general terms and indicates that an attack on the problem by way of engineering fundamentals, regarding economics as a collateral matter, should be appealing to research-minded individuals and should be conducive to a more harmonious relationship between advocates of close and wide spacing.

It is believed that the results of the theoretical study, when published, will represent a plane of common understanding for students of the problem and will stimulate further interest and research on the important subject of well spacing.

Drilling-Fluid Research

The composition and control of drilling fluids and the effect of completion fluids on well productivity are problems of continuing importance that have been studied for the past decade. During this period Bureau engineers and others have repeatedly pointed out the damage that may be caused to the productivity of wells by invasion of filtrates from water-base drilling fluids into oil-bearing formations. Accordingly, in recent years there has been growing realization among petroleum engineers of the importance of using completion fluids that will not reduce the permeability of oil-bearing formations to oil.

As part of a study of well-completion practices begun during the year, an analysis is being made of completion data for several wells in a field in the San Joaquin Valley, Calif., to develop comparative information on the effect of different completion fluids on the productivity of the wells. Evaluation of the effect of completion drilling fluids usually has been difficult because a well can only be drilled once, but the foregoing wells were completed with a clay-water drilling fluid and later plugged back and redrilled as slant holes using oil-base drilling mud as the completion fluid. The redrilled holes were bottomed about 75 to 100 feet from the original holes. In every instance where the well was producing from the black-oil zone, plugging back and redrilling with an oil-base drilling fluid resulted in a substantial increase in production. The completion records of these wells are notable examples of the reduction in permeability caused by the invasion of filtrates from water-base muds into a productive sand. The permeability, as calculated from productivity data for one of the wells completed originally with clay-water mud, was found to be 1 millidarcy. In contrast, the calculated permeability after redrilling the well with oil-base mud was about 23 millidarcys. In general terms this means that the reservoir energy consumed per barrel of oil produced is only about one-twenty-third as much in the redrilled well as that consumed in the original well. These calculated data offer a measurable means of understanding the physical change in reservoir-flow characteristics caused by the detrimental effect of a clay-water mud compared with an oil-base mud on the productivity of a sand reservoir. They emphasize the importance of proper well-completion practices as a means of obtaining greater ultimate recovery of oil. A report on this field study of well-completion practices is being prepared for publication. It will include also the results of previous laboratory tests showing the contaminating effect of different fluids on the permeability of core samples to oil.

Work was continued on the correlation of water saturations of cores obtained by core analysis with those obtained by capillary methods, including: (1) Displacement

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of interstitial water by air; (2) displacement of air by mercury and; (3) evaporation of liquid from the pore space. The different procedures have been improved, and apparatus now being assembled will make it possible to facilitate obtaining additional data in these correlation studies.

Quebracho Substitutes

Since 1949 Bureau engineers in the San Francisco laboratory have tested some 75 natural substances and byproduct materials to determine their suitability as substitutes for quebracho for controlling the filter properties and viscosity of clay-water drilling fluids. This search for quebracho substitutes has been made in the interest of national security, in cooperation with the Department of Agriculture and many industrial firms, to explore the possibilities of providing an adequate replacement material in an emergency that would cut off or drastically reduce importations of quebracho from South America. Several inexpensive domestic materials available in large quantities have been found to be suitable substitutes for quebracho under ordinary conditions of drilling but inferior to quebracho when subjected to contamination by salt water and elevated temperatures. These tests provide the basis for a report now being prepared for publication, which will include a discussion of the adequacy of the most effective substitute materials and their availability.

Equipment for Sampling and Analyzing Fluids from Deep Wells

The advent of deeper drilling in the Rocky Mountain area has necessitated changes in existing equipment and installation of new equipment in the laboratory and the field truck to cope with the higher reservoir pressures and temperatures and the more volatile reservoir fluids that are being discovered. With these changes in the equipment, wells with depths to 17,000 feet can now be sampled and tested, and volatile liquid-phase and gas-condensate samples can be analysed. Thus, continued effective aid can be given in the efforts to obtain maximum recoveries of these vital petroleum resources.

Sulfur Recovery

The availability of hydrogen sulfide as a basis for producing elemental sulfur was studied again in view of the discovery of five new sources of the gas.8/ Over 275,000 long tons of sulfur have been produced from hydrogen sulfide in Wyoming by July 1952.

Helium-Tracer Studies

Petroleum engineers at the Amarillo Helium Plant continued to provide consulting and field-engineering assistance to private companies interested in using helium as a tracer in petroleum and natural-gas reservoirs. In addition, the Bureau cooperated with another Government agency in analyzing samples and providing technical assistance in a helium-tracer project in California.

8/ Espach, R. H., Sulfur in Wyoming: Paper before Rocky Mountain Section, Am. Assoc. Petrol. Geol., Feb. 29, 1952.

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Field Studies

Survey of Secondary-Recovery Operations in California

A survey of secondary-recovery operations in California was completed with publication of a report in two parts[9] describing 15 representative fluid-injection projects in the San Joaquin Valley, Los Angeles Basin, and Coastal oil fields. These selected fields include oil-productive formations typical of upper Pliocene through Oligocene strata ranging in depth from 1,400 to 11,000 feet below sea level and producing various black oils and condensate ranging from 19° to 60° A.P.I. gravity. Stimulative methods of production include pressure maintenance by gas injection, low-pressure gas injection, water injection, and waste-water disposal.

The report outlines the principal problems associated with secondary-recovery operations in California and discusses the economic possibilities of these operations. It describes the development and operation of the individual fields and the characteristics of the reservoirs and associated fluids, also includes their production histories, and analyzes the effects of gas injection and water injection in sustaining production and improving ultimate recovery of the fields. In reservoirs where the results were unfavorable, an analysis is given of the factors and conditions that adversely affected the efficiency of the injected fluid in displacing oil from the reservoir rock or in augmenting the available expulsive reservoir energy.

It is believed that a description of the techniques applied to these problems and an evaluation of the results obtained may serve as norms for development and economic operation of other similar projects.

A paper summarizing the main problems associated with fluid injection in California and the status and future possibilities of secondary recovery in this State was presented before the Drilling and Production Division, Third World Petroleum Congress, The Hague, 1951, and published in the proceedings of the Congress.[10]

In a more detailed paper on the subject presented at the Spring Meeting, Interstate Oil Compact Commission, Phoenix, Ariz., May 9-10, 1952,[11] emphasis was placed on the problems arising from the widespread occurrence of faulting; thick, heterogeneous sand sections; lensing; and very viscous oils, especially in the shallower fields in the State. The economic possibilities of water-flooding selected fields in California also were discussed in the light of an analysis of the results obtained in several large-scale field projects and of a study of the recovery obtained by natural water drive in the Wasco field, where, under unusually favorable conditions,

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9/ Loomis, A. G., Fried, A. N., and Crowell, D. C., Recovery of Oil in California by Secondary Methods, - Part I, San Joaquin Valley Oil Fields: Bureau of Mines Rept. of Investigations 4886, 1952, 64 pp.
_____, Recovery of Oil in California by Secondary Methods, - Part II, Los Angeles Basin and Coastal Oil Fields: Bureau of Mines Rept. of Investigations 4887, 1952, 46 pp.

10/ Loomis, A. G., and Shea, G. B., Secondary Recovery of Oil in California: Proc. 3d World Petrol. Cong., The Hague, Section II, Drilling and Production, 1951, pp. 608-616.

11/ Loomis, A. G., Summary of Secondary Recovery Operations in California: Presented before Secondary Recovery and Pressure Maintenance Advisory Committee, Spring Meeting Interstate Oil Compact Commission, Phoenix, May 9-10, 1952.

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including a relatively thin, continuous formation, uniform advance of edgewater, and low oil-water viscosity ratio, about 50 percent of the oil in place was recovered.

Survey of Water Flooding in Oklahoma

Water flooding to recover additional oil from partly depleted oil-bearing sands was first tried in Oklahoma in 1931. Powell and Johnston[12/] report that on January 1, 1950, 200 projects had been begun or authorized in Oklahoma and that more than 18,000 productive acres had been flooded. At that time water-flooding operations in the State were yielding over 3 million barrels of oil annually through injection of about 42 million barrels of water. The development of new projects at an unprecedented rate foreshadows a much larger rate of production by secondary-recovery methods.

The spread of water-flooding operations throughout the State is particularly noteworthy. For many years these operations were concentrated in Nowata and Rogers Counties and restricted to the Bartlesville sandstone. There now are flooding projects in 25 of the 49 oil-producing counties in Oklahoma in more than two dozen oil sands.

Survey of Water Flooding in Northeastern Kansas

The rapid expansion of secondary-recovery operations throughout the Midcontinent area has provided a continuing strong demand for information regarding the results that are being obtained by these operations in different areas, fields, and producing formations. To keep pace with this demand, a survey of water-flooding operations in Franklin, Miami, Linn, and Anderson Counties, Kans., was begun late in the year. The study will include about 60 projects in the four counties.

Nowata County, Okla.

Bureau of Mines engineers arranged a tour of typical water-flooding projects in Nowata County, Okla., for 350 members and guests of the Kansas-Oklahoma Water Flood Operators, Northeast Oklahoma Oil Producers, Inc., and the Kansas section of the American Institute of Mining and Metallurgical Engineers. The tour was designed to stimulate interest among the operators in the shallow oil fields of northeast Oklahoma and eastern Kansas in secondary-recovery methods of oil production. It also gave operators of water-flooding projects an opportunity to compare different equipment and techniques being used. Figure 1 shows part of the group that made the tour listening to a Bureau of Mines engineer describe one of the projects visited.

A report[13/] describing the projects included in the tour was released the same day and very materially added to the success of the tour. Powell and Eakin point out in this report that since 1935 Nowata County has been the area of greatest water-flooding activity in the Midcontinent. Figure 2 shows the estimated oil-production

12/ Powell, John P., and Johnston, Kenneth H., A Survey of Oil Production in Oklahoma by Water Flooding, Part I. Nowata, Rogers, and Craig Counties: Bureau of Mines Rept. of Investigations 4831, 1952, 160 pp.
Powell, John P., and Johnston, Kenneth H., A Survey of Oil Production in Oklahoma by Water Flooding, Part II. Counties Other Than Nowata, Rogers, and Craig: Bureau of Mines Rept. of Investigations 4832, 1951, 142 pp.

13/ Powell, John P., and Eakin, J. L., Water Flooding in Nowata County, Okla., Oil Fields: Bureau of Mines Rept. of Investigations 4896, 1952, 49 pp.; also in condensed form in Producers Monthly, vol. 16, No. 9, July 1952, pp. 29-39.

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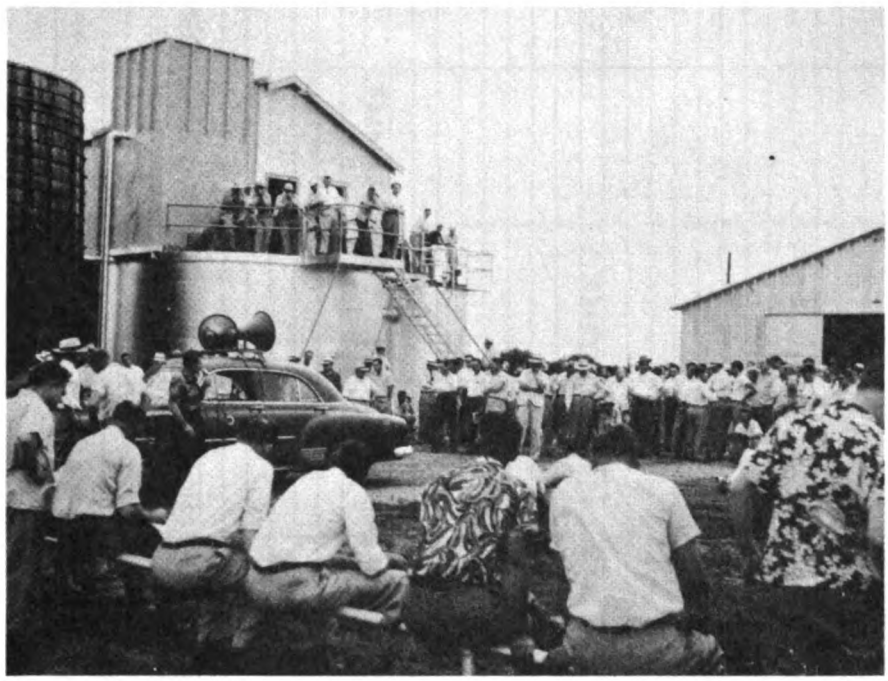

Figure 1. - Water-flood operators and engineers at project during tour of water-flood plants in Nowata County, Okla.

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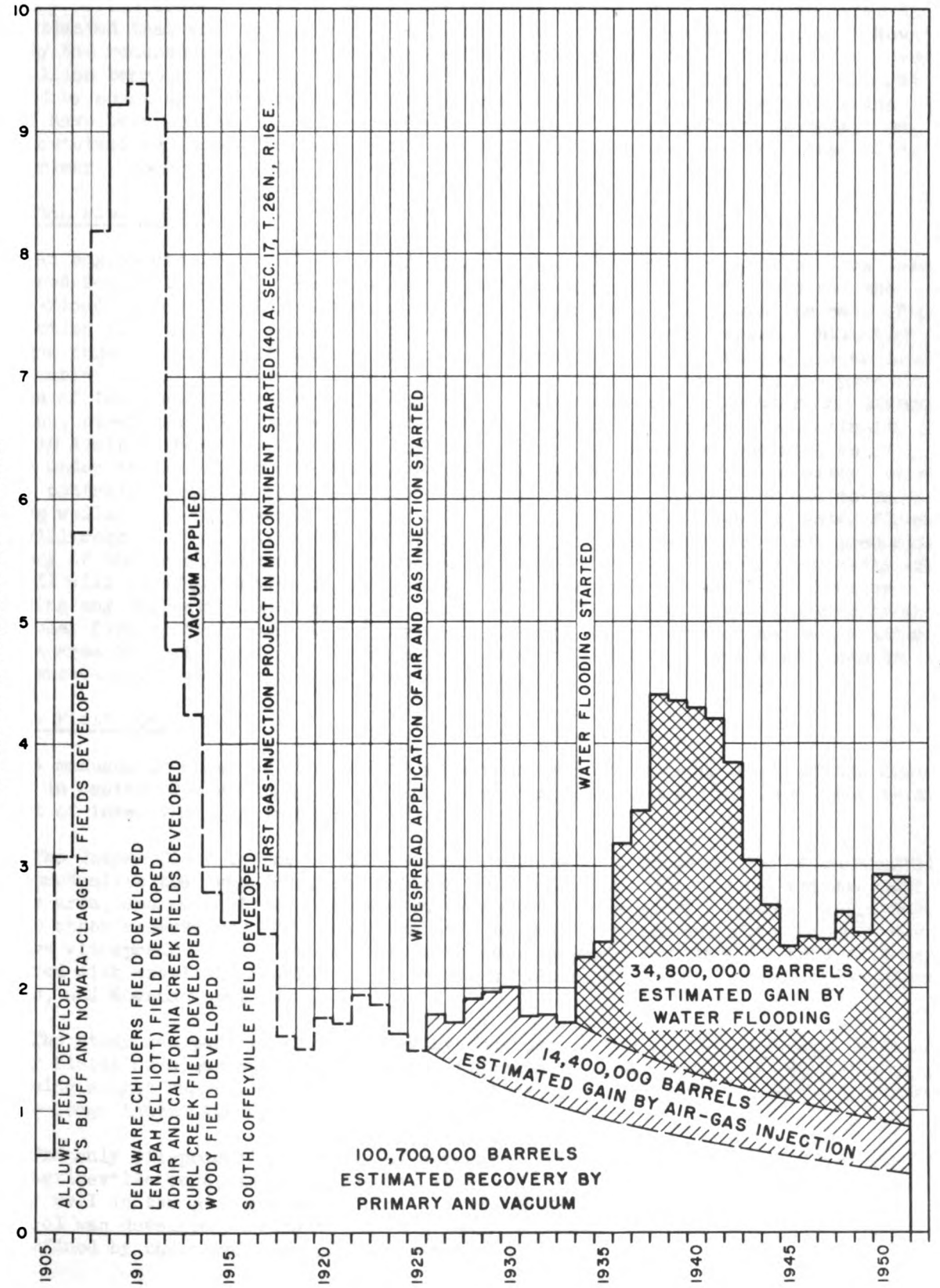

Figure 2. - Production history of Nowata County, Okla.

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history of the county based on imcomplete records before 1925. From this curve it is estimated that the increased oil recovery as a result of water flooding in Nowata County had reached nearly 35 million barrels at the end of 1951. In addition, over 14 million barrels of oil had been gained by air and gas injection. Thus, the oil gained by secondary-recovery methods amounts to about half as much as that which would have been obtained throughout the life of the field by primary methods. On some outstanding leases the recovery by secondary methods has been more than twice the primary recovery.

Healdton Field, Okla.

An engineering study of the Healdton oil field, Carter County, Okla., now being prepared for publication, describes the production history of that field and the water-flooding possibilities of some of the Healdton sands. Although the rate of oil production in this field has been sustained by infill drilling, vacuum application, and gas injection, indications are that, when present operating methods are no longer profitable, nearly two-thirds of the original oil will still remain in the pore spaces of the Healdton sands. Although many of the sands are lenticular and discontinuous, stratigraphic studies and movements of injected gas prove the continuity of sand in limited areas. Laboratory flooding tests on core samples and studies of areas under the influence of natural water drive indicate that flooding water, carefully controlled, can be made to displace nearly half of the remaining oil to producing wells. The economical recovery of oil from any lease or area by water flooding will require a consideration of the geological conditions and the past production history of the area. The oil and water saturation of the sand and the viscosity of the oil will be of paramount importance in considering the advisability of water flooding any property. Because of structure and sand lensing, some departure from a regular five-spot pattern may be advisable. Tests on subsurface samples of water in the area indicate that, if adequate volumes are available, these waters can be used successfully with little chemical treatment.

Quapaw Field, Okla.

A manuscript covering the results of a petroleum-engineering study of the Quapaw field in eastern Osage County, Okla., has been completed and will be published as a report of investigations in fiscal 1953.

The Quapaw field is one of the smaller pools in an extensive area of Bartlesville-sand production that was developed between 1906 and 1916. The pool is representative of the area, and much of the information developed in the study is equally applicable to the other reservoirs. The study was made to provide reservoir data that may aid in more widespread application of intensive secondary-recovery methods that have been employed with excellent results in the Bartlesville-sand fields of nearby Washington, Rogers, and Nowata Counties.

The study was particularly appropriate because of the intense interest in Osage County fields as areas suitable for water flooding. Leases in eastern Osage County are being sought eagerly by water-flood operators, and nine permits have been issued by the Osage Indian Agency for water-flooding projects in the area.

The only oil-producing stratum of commercial significance in the Quapaw pool is the Bartlesville sand, which is reached at depths of 1,600 to 1,800 feet. The discovery well in the pool was completed in July 1914 at a total depth of 1,762 feet. The pool was developed during the next 5 years, and the proved area of 3,095 acres was defined by the completion of approximately 275 wells during this period.

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Solution-gas drive was the primary displacement mechanism in the reservoir during its operation by primary-production methods. The natural reservoir energy was dissipated rapidly, however, and it is estimated that approximately 6,520,000 barrels of oil, equivalent to only 15.3 percent of the original stock-tank oil in place, was recovered by primary-production methods. Secondary-recovery methods, consisting of vacuum and restricted gas-injection operations resulted in the recovery of an additional 1,520,000 barrels of oil.

Water flooding appears to be the only known method of production that can effect the recovery of a substantial part of the oil remaining in the reservoir. Economic limitations will not permit development of the entire reservoir, but the Bureau's study indicates that an additional 8,000,000 barrels of oil can be recovered by efficient water flooding.

Flat Rock Field, Okla.

A petroleum-engineering study of the Flat Rock field in Osage County, Okla., has been initiated at the suggestion of the Indian Agency at Pawhuska. This field includes approximately 6,365 oil-productive acres on which 858 oil-producing wells were drilled. Available production data indicate that about 22 million barrels has been produced from 713 Bartlesville-sand wells, about 3 million barrels was produced from 105 Wilcox-sand wells and less than 1/4 million barrels of oil has been recovered from the remaining 40 wells producing from five other reservoirs. In this area the Bartlesville sand consists of an upper zone of interbedded sand and shale and a lower main sand body, the upper part of which is oil bearing. Bottom-hole water has been noted in the field at depths ranging from 660 to 710 feet below sea level. Two pilot water-flooding projects now are operating in the Barltesville sand, but without marked success. Although there is no evidence of a definite water drive in the Bartlesville sand, most of the wells produce water with the oil. Analyses of several cores obtained during water-flood development show oil saturation ranging from 20 to 40 percent and water saturations from 30 to 40 percent.

Southwestern Part of K.M.A. Field, Tex.

Under a cooperative agreement with the North Texas Oil and Gas Association, Bureau of Mines engineers completed an engineering study of the southwestern part of the K.M.A. oil field, Wichita and Archer Counties, Tex. The report[14/] is a comprehensive analysis of the K.M.A. reservoir from the time of discovery, 1931, to the projected date of abandonment. The gas-pressure-maintenance program carried on in this field since 1940, was analyzed and the feasibility of recovering additional oil by water flooding was investigated.

This report deals with an area of about 12,500 acres developed by drilling 700 wells. The K.M.A. Strawn formation reservoir is of Pennsylvanian age and was found to be oil-productive at an average depth of 3,750 feet. The K.M.A. structure is a complex anticline with a maximum closure of 250 feet, and the Strawn formation in the K.M.A. field is composed of sediments that grade from limestone through sandy lime and limy sand to sandstone with streaks of shale. Two distinct zones of varying thickness within the Strawn formation are oil productive.

The initial volume of oil in place in the K.M.A. reservoir was calculated to be 168.1 million barrels of stock-tank oil. The original reservoir pressure was estimated to be 1,750 lb. per sq. in. From analyses of subsurface fluid samples, the

14/ Dobyns, Rollie P., Ayers, Marion L., and Lewis, Roger E., Petroleum-Engineering Study of K.M.A. Reservoir, Southwestern Part K.M.A. Oil Field, Wichita and Archer Counties, Tex.: Bureau of Mines Rept. of Investigations 4892, 1952, 88 pp.

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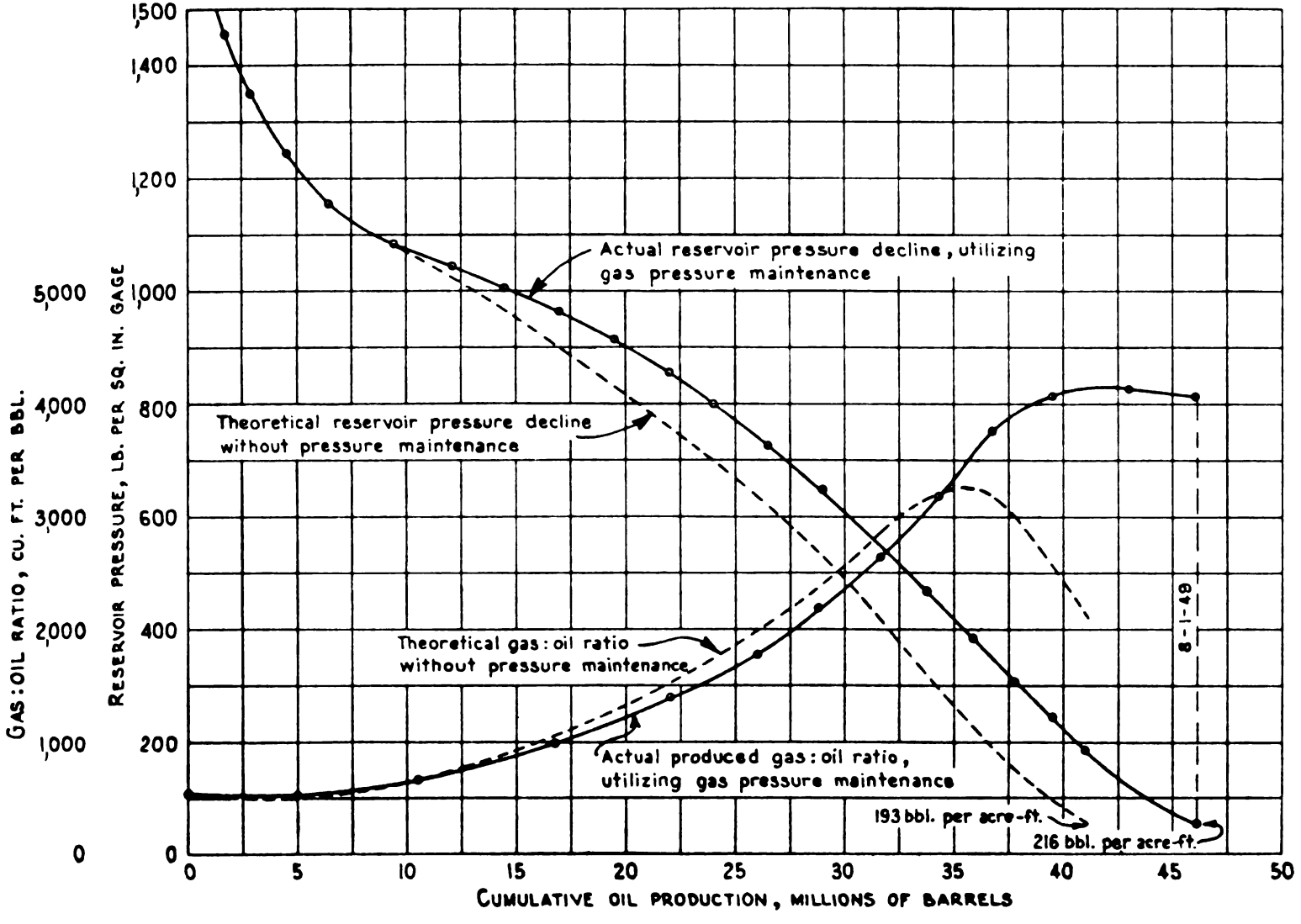
GAS:OIL RATIO, CU. FT. PER BBL.
RESERVOIR PRESSURE, LB. PER SQ. IN. GAGE
CUMULATIVE OIL PRODUCTION, MILLIONS OF BARRELS
Actual reservoir pressure decline, utilizing gas pressure maintenance
Theoretical reservoir pressure decline without pressure maintenance
Theoretical gas:oil ratio without pressure maintenance
Actual produced gas:oil ratio, utilizing gas pressure maintenance
193 bbl. per acre-ft.
216 bbl. per acre-ft.
8-1-48

Figure 3. - Comparison of actual reservoir performance utilizing pressure maintenance and calculated theoretical reservoir performance without pressure maintenance, K.M.A. reservoir, southwestern part of K.M.A. field, Wichita and Archer Counties, Tex.

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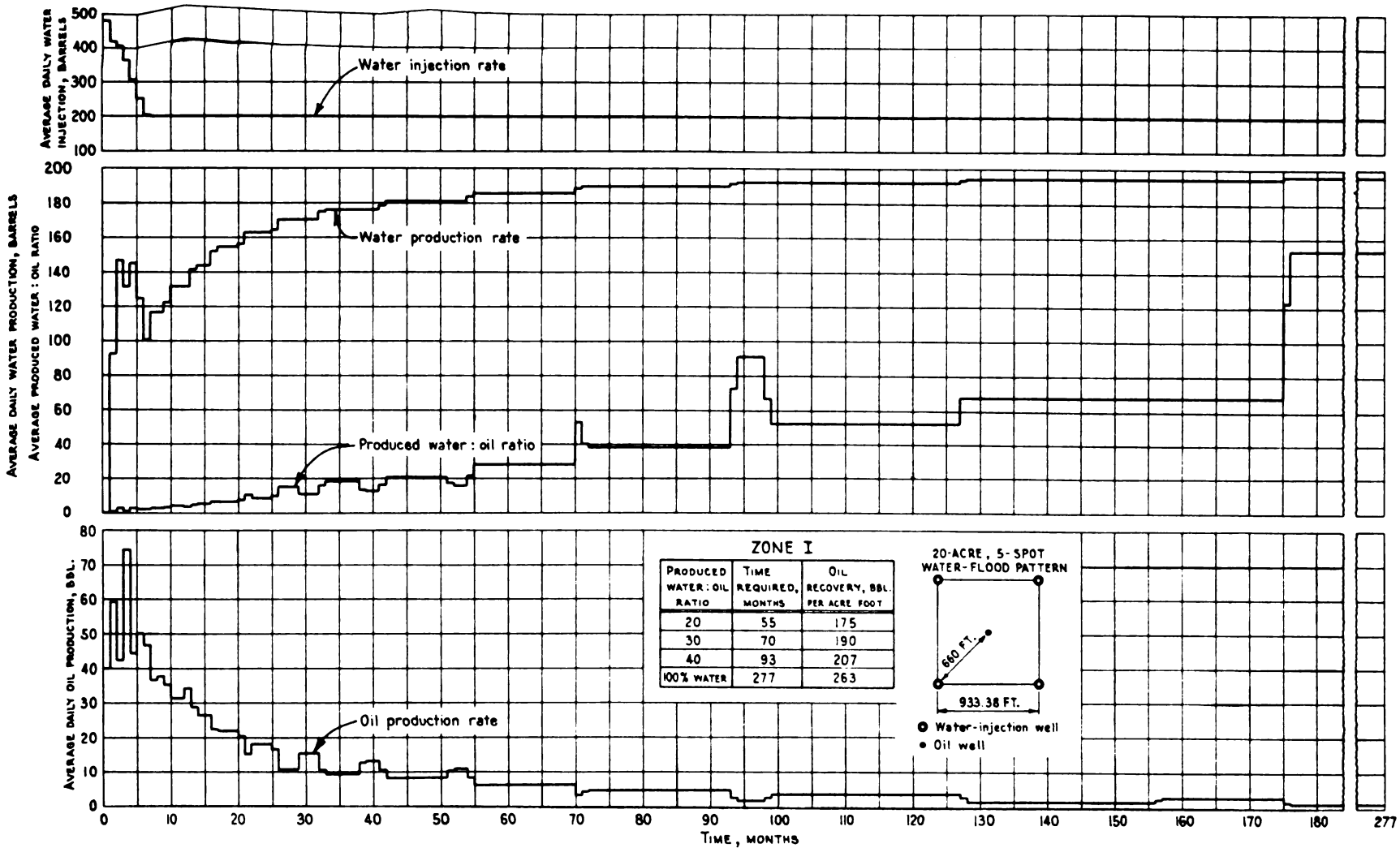
Average daily water injection, barrels
Water injection rate
Average daily water production, barrels
Average produced water : oil ratio
Water production rate
Produced water : oil ratio
Average daily oil production, bbl.
Oil production rate
Time, months
ZONE I
Produced water : oil ratio | Time required, months | Oil recovery, bbl. per acre foot
20 | 55 | 175
30 | 70 | 190
40 | 93 | 207
100% water | 277 | 263
20-acre, 5-spot water-flood pattern
660 ft.
933.38 ft.
Water-injection well
Oil well

Figure 4. - Calculated theoretical production history of one 20-acre, five-spot water-flood project, zone I, K.M.A. reservoir, southwestern part of K.M.A. field, Wichita and Archer Counties, Tex.

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reservoir oil at initial conditions was estimated to have a saturation pressure of 1,300 lb. per sq. in., and a solution gas-oil ratio of 525 cu. ft. per barrel. The gravity of the oil was about 43° A.P.I.

A rapid decline in reservoir pressure during the early life of the field caused the operators to consider a gas-pressure-maintenance program. In the latter part of 1939 a cooperative organization was formed to return gas to the reservoir. Approximately 27 percent of the cumulative volume of produced gas has been returned to the reservoir by August 1, 1949.

An increase in oil recovery of approximately 5,000,000 barrels, as a result of the pressure-maintenance program, was estimated by comparing the actual recovery of 46,107,738 barrels to August 1, 1949, with the calculated theoretical recovery of 41,000,000 barrels without pressure maintenance (fig. 3). The ultimate recovery by present methods of production is estimated to be 53 million barrels of stock-tank oil, which represents 31.5 percent of the initial oil in place.

The large volume of oil remaining in the K.M.A. reservoir has encouraged investigating the possibilities of water flooding this reservoir. The theoretical performance of a 20-acre, five-spot-pattern water flood (using average field-wide physical characteristics of the formation) was calculated (see fig. 4 for zone I), and the results of these calculations indicate that approximately as much additional oil could be recovered by water flooding as had been recovered to August 1, 1949. The engineering and operating aspects of injecting water into the reservoir also are discussed in the report.

The oil operators should derive a direct benefit from this report, as the analysis of the gas pressure-maintenance program can serve as a yardstick for developing similar reservoirs. In addition, the water-flood calculations indicate the susceptibility of the reservoir to additional secondary-recovery methods by injecting water that could possibly increase the oil recovery from this reservoir by 35,000,000 barrels.

North and West Central Texas

A preliminary investigation into the water-flooding activities in North and West Central Texas was begun during the year. Since the publication of Report of Investigations 4250[15/] and the North Texas Oil and Gas Association report,[16/] approximately 130 new water-flooding projects have been begun in 22 counties. Engineering data concerning the results obtained from these new water floods, as well as the old ones previously reported, will be collected and compiled for the benefit of the oil operators. The data will be kept as current as possible, and reports for publication will be prepared on selected water floods from the data available in the files.

Cabin Creek Field, W. Va.

An engineering study of gas-injection operations and the effect in recovering more oil has been made on a part of the Cabin Creek field in West Virginia. Gas-injection project 4 has an oil-productive area of 1,669 acres, and the average

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15/ Guthrie, Robert K., Amyx, James W., and Taliaferro, D. B., Jr., Secondary Recovery of Oil by Water Flooding in Fields of North Texas: Bureau of Mines Rept. of Investigations 4250, 1948, 158 pp.

16/ North Texas Oil and Gas Association, A Survey of Secondary Recovery of Oil by Water-Flooding in the Fields of North Texas: March 1950, 144 pp.

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thickness of the oil-bearing Berea sandstone is 14.7 feet. The study shows that the cumulative production at the time the limit of economic production is reached would be 5,650,000 barrels of oil; approximately 1,660,000 barrels of this oil - a 42-percent increase in ultimate oil recovery - would be the result of gas-injection operations.

The development of that part of Cabin Creek field was begun in 1917 and by 1935, the year gas injection was begun, 50 wells had been completed. In 1944, 11 gas-injection wells and 64 oil-producing wells were operating in the part of the field designated as project 4. In those wells the oil-bearing stratum occurs at depths ranging from 2,914 to 3,410 feet below the surface of the ground. By the end of 1944, 2,677,598,000 cubic feet of natural gas had been injected into the project reservoir.

A report[17] covering project development, structural conditions, operation, oil-production history, and reservoir analysis of the portion of the Cabin Creek field studied was completed.

Special Field Problems

Finding Abandoned Wells

The study of methods of finding abandoned wells that have been improperly plugged was completed, and a report[18] was published which provides a new approach to this problem that has been a constant source of expense, waste, and irritation to secondary-recovery operators in old fields. Although no positive method was developed for finding wells from which all the pipe had been removed, it usually is possible to find metal scrap and boiler cinders around the location of these wells with a mine detector. After the search has been localized in this way the exact location of the well often can be found by probing, or by studying surface evidence. It was found that wells that still contain some pipe usually can be found readily with a mine detector and a dip needle.

Subsurface Measurements to Determine Physical Properties of Petroleum Reservoirs (Selective Plugging)

Completion of the small-diameter (1-3/4-inch), liquid-level gage and the small-diameter (1-3/4-inch) well-bore caliper for use in the study of selectively plugging water-input wells makes available the instruments necessary for obtaining input profiles of oil-producing formations even though the wells are completed with 2-inch tubing cemented in place.

The liquid-level gage can be used to measure 1/2-inch changes in the level in a well. The well-bore caliper can measure four radii, 90° apart, over a range of 4 to 18 inches with an accuracy of ± 1/4 inch. The caliper arms can be opened and closed by remote control to allow withdrawal of the instrument from a well through 2-inch tubing. Both instruments are operated on a single, armored, electrical cable with suitable telemetering equipment at the surface to indicate the readings.

The input profile on a water-input well is measured by first shutting the well in long enough to allow the pressure in the sand around the well and the height of the fluid column in the well to reach equilibrium and then forcing the water remaining in the well into the sand under a constant bottom-hole pressure. This is done

17/ Magee, Joe N., and Taylor, Sam S., Petroleum-Engineering Study of Gas Injection in the Cabin Creek Field, Kanawha and Boone Counties, W. Va.: Bureau of Mines Rept. of Investigations 4899, 1952, 24 pp.

18/ Hamontre, H. C., Locating Abandoned Wells: World Oil, March 1952, vol. 134, No. 14, pp. 187-190.

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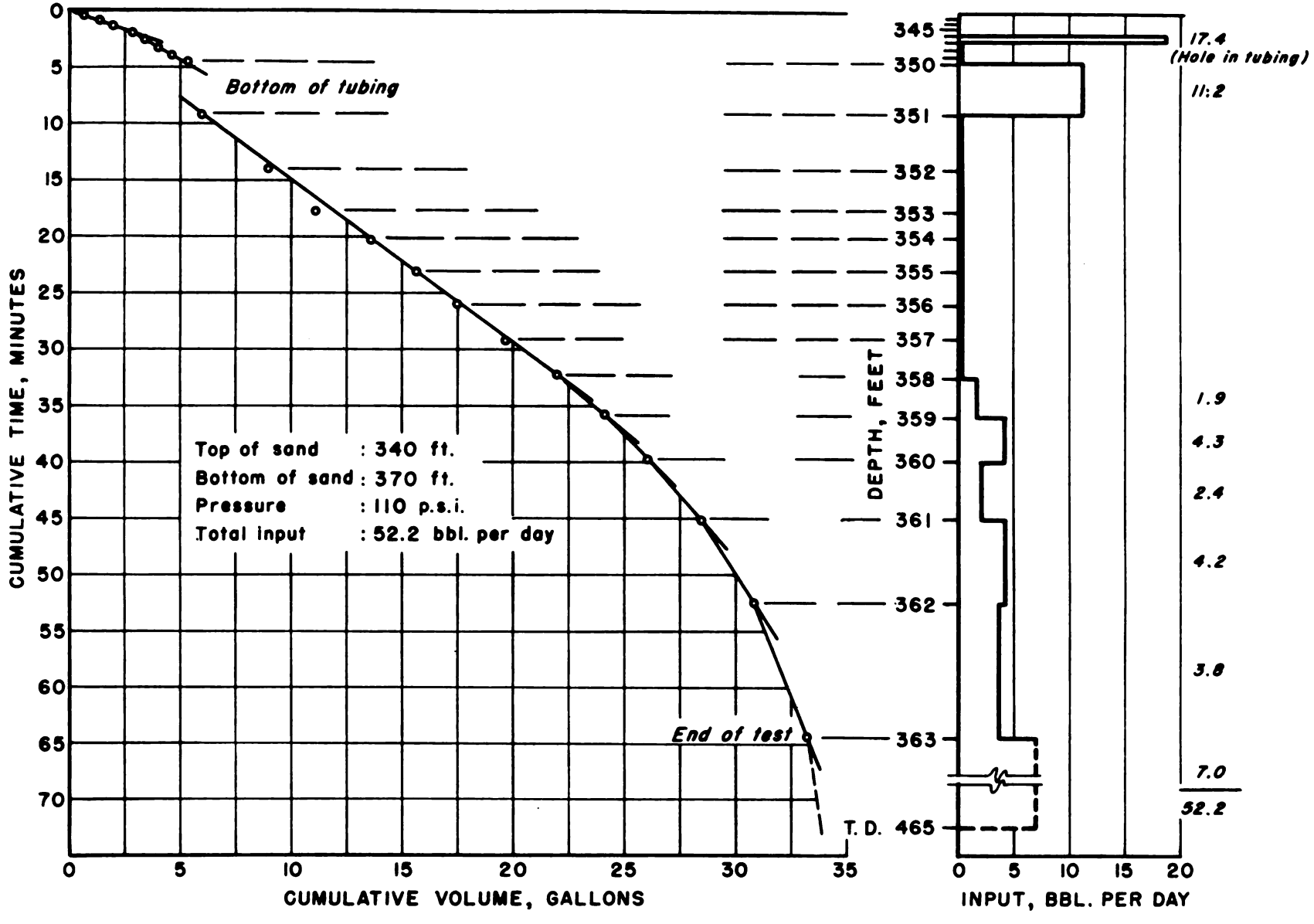

Figure 5. - Water-input profile.

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by admitting gas under pressure at the wellhead under gradually increasing pressures to offset the reduction in bottom-hole pressure resulting from the continuous decrease in the weight of the fluid column in the well. During this procedure the liquid level in the well is followed closely with the liquid-level gage, and the rate of fall of the liquid level through each foot of depth is recorded. If the well is of uniform bore the change in the rate of fall of the liquid level from one foot to the next indicates the amount of fluid that was entering that foot of sand. Actually the diameter of the bore of most wells varies; and, as this variation affects the input-profile measurement, it is necessary to caliper the well and make the proper corrections.

By running input profiles before and after selective-plugging operations or other remedial work in input wells it is possible to evaluate the work immediately rather than wait for weeks for the effect of the work to be reflected in the behavior of the surrounding oil-producing wells.

Figure 5 presents graphically the data obtained by using the liquid-level gage and bottom-hole caliper in making a water-input profile on one typical water-input well.

Selective Plugging of Air-Gas Injection Wells

On many older gas-injection projects in the Pennsylvania area, ratios of injected gas to produced oil have reached values of over 30,000 cu. ft. per barrel. Under present economic conditions, these projects must be abandoned unless means are found to reduce the amount of gas required to produce the oil. One of the approaches to this problem is the development of means of "selective" plugging to reduce, in the injection well, the flow of injected gas into the layers or beds of highest permeability, which may be presumed to be depleted of recoverable oil, but without appreciably reducing the fluid conductivity of the less permeable beds. Diversion of the gas thus saved to the less permeable beds then should increase their rates of oil production.

From earlier experience with this problem it was decided to investigate means by which an aerosol (smoke) could be generated opposite the sand face in an injection well. The reaction of titanium tetrachloride vapor with water vapor to form titanium dioxide smoke appeared promising. A laboratory apparatus was built in which the smoke could be generated under pressure and flowed into four core samples under conditions similar to those in the sand around operating wells. The four core samples used in a test were chosen to have different permeabilities and to cover a permeability range similar to that existing in local reservoirs. Of 15 test runs made with titanium dioxide smoke, 14 demonstrated an excellent selectivity of plugging. A smoke generator has been designed for use in injection wells equipped with 2-inch or larger tubing, and a location for a field test has been obtained through the courtesy of the Quaker State Oil Refining Corp., Bradford, Pa.

Conditioning Water for Subsurface Injection

A manuscript on conditioning water for secondary-recovery operations in Midcontinent oil fields has been completed and will be published as a Bureau report of investigations. The report points out the importance of properly conditioning water and discusses the particular methods of conditioning used in the Midcontinent oil-producing area. Field methods of making corrosion tests and chemical analyses are described briefly.

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Nine of the plants that were studied are described, and the methods used and the results obtained are presented. The conclusions drawn from the study of 24 water-treating plants stress the importance of the following in the design and operation of water-treating plants:

1. Careful analysis and study of waters available for injection before design and construction of a conditioning plant and injection system.

2. Simplicity in plant design and in the choice of treating methods insofar as is practical, considering the characteristics of the water to be treated.

3. The relative damage caused by corrosion of metallic equipment, as compared to the damage caused by plugging of the pores of the oil-producing formations.

4. Frequent routine water analyses and close control of plant operation.

5. The use of adequate baffles in sedimentation ponds and tanks.

6. Early detection and control of organic matter.

A meter was designed and constructed to measure the dissolved-oxygen content of water. The meter is both rapid and accurate in the quantitative determination of dissolved oxygen in electrolytes, such as oil-field waters, and therefore is much preferred to the commonly used Winkler method.

Resistivity of Formation Waters in North Texas

A study of the resistivity of subsurface formation waters in North Texas was begun and a manuscript is being prepared. This study is in cooperation with the North Texas Oil and Gas Association and will increase the reliability of quantitative interpretations of electric logs in the North Texas area. A total of 638 water samples were collected from 14 counties in the North Texas area, and the resistivity of these water samples was either measured directly with a resistivity meter or calculated indirectly from chemical analysis. This resistivity information will be beneficial to the oil operators because it will determine one of the main unknown factors in applying mathematical equations to the quantitative interpretation of electric logs.

Water Flooding Studies

Results of studies of reservoir and wax-precipitation temperatures relating to possible wax deposition in the reservoir of the Bradford oil field were reported.19/ These studies showed Bradford Third-sand temperatures range from 59.7° F., at 1,150 feet to 71.9° F., at 2,040 feet. Injection-well temperatures measured during water injection showed that the temperature of the water entering the sand was 11.5° F. lower than reservoir temperature before injection. The maximum cooling in the formation 200 feet from the injection well was 2.1° F. The temperature at which wax begins to precipitate from the crude oil ranged from 51° to 67° F. The study indicated that solid wax might be deposited in the reservoir, as injection of cold water

19/ Sayre, Allyn T., Jr., and Wertman, W. T., Effects of Water Flooding on Reservoir Temperatures and Wax Precipitation in the Bradford, Pa., Oil Field: Bureau of Mines Rept. of Investigations 4842, 1952, 34 pp.; also Producers Monthly, vol. 16, No. 3, January 1952, pp. 16-24 and vol. 16, No. 4, February 1952, pp. 11-21.

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not only causes a reduction of reservoir temperature but also alters the composition of the reservoir oil by absorbing light hydrocarbon constituents from the oil. These findings indicated a need for greater knowledge of the composition of Bradford crude oil, particularly the individual compounds comprising the range through nonanes. A complete analysis was made and published[20] by the Synthetic Fuels Research Branch, Region VIII, Bureau of Mines, Bruceton, Pa.

Subsequent laboratory tests were conducted to determine the effects of the low-temperature water flooding using unconsolidated sand packed in tubes and radial sandstone cores. The tests showed that the efficiency of a water flood depends upon the viscosity ratio of the displaced liquid (oil) and the displacing liquid (water). The viscosity ratio increases as the temperature of the liquids decreases. The change in viscosity ratio is greater at temperatures below the wax-precipitation temperature because wax crystals form in the oil. An appreciable decrease in oil recovery at water breakthrough occurs when such conditions exist. Oil recovery during the subordinate phase (after water breakthrough) of low-temperature water floods decreases for normal volumes of water throughput. If carried to extremely high water-oil ratios, the oil recoveries of water floods conducted at temperatures 8° F. above or below the wax-precipitation temperature of the crude oil will be the same.

Laboratory tests were made to study the effects of liquid carbon dioxide on Bradford crude oil. When equal parts of the two liquids were associated and the phases (extract and raffinate) separated under pressure and depressured, it was found that 23 to 30 percent of the original oil volume had been extracted by the liquid carbon dioxide. Distillation tests and specific-gravity and viscosity determinations on the original crude oil, the extract, and the raffinate showed that, apparently, extraction occurred according to molecular size rather than molecular type, with the greatest extraction occurring in the lighter hydrocarbon (gasoline) range.

Flowing of Oil Wells on Gas-Injection Projects

The study of the feasibility of flowing the producing wells on gas-injection projects was continued. In the Appalachian area some 200 wells are equipped with small-diameter siphon-type flowstrings designed to produce periodic flow at production rates between 0.1 and 5.0 barrels of liquid daily per well. Records of injected and produced gas and produced liquids have been accumulated on these wells over several years of operation to show that flowing produces operating economies and increases production efficiency. During 1951-52 collection of these operating data was narrowed to two groups of leases.

In addition to the detailed study of leases equipped to flow, rough analyses made of three other gas-injection projects indicated that it would be feasible to convert the wells on two of these projects to flowing.

Also, work was continued on a flowing-well, gas-injection project that was begun in 1951 in Anderson County, Kans. Frequent measurements of individual well-production rates were made to determine the effect on flowing imposed by different controlled operating conditions. The improvised controllers necessary to flow these wells with a minimum of produced gas have been improved and now require little attention. The operator intends to water flood this property within 2 years. The build-up of gas saturation in the sand during the present flowing period is expected to increase ultimate oil recovery by water flooding, an effect that has been observed in laboratory and field tests.

20/ Feldman, Julian, Scarpino, Lawrence, Pantazoplos, Gus, and Orchin, Milton, Composition of Crude Oil from the Bradford Field, Pa.: Producers Monthly, vol. 16, No. 6, April 1952, pp. 14-16.

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Shooting Oil and Gas Wells with Explosives

Results of the experimental program on well shooting during the summer of 1950 were published.21/ Inasmuch as the program was curtailed during 1950, the test results are not complete. However, the experimentally determined relation of height of stemming to strain produced in rock by unit explosive charges shows that stemming has as large an effect on rock breaking by explosives as any of the variables so far investigated. One series of tests in which the length of cylindrical charges was varied while their diameters were held constant demonstrated that the strain produced in the rock at any point around the charge was affected only by that section of a cylindrical charge that is opposite the point and whose length is equal to 0.4 of the distance from the point to the charge. This basic information is necessary to an understanding of well shooting and to the design of future experiments.

The strength and elastic properties of oil-bearing reservoir rocks are being studied in the Bureau's College Park, Md., Station. The testing of several hundred core samples of nine oil-bearing and several non-oil-bearing sandstones indicates an interrelationship of strength and elastic properties of the specimens with their scleroscope hardness. By resolving this systematic relationship in more detail, physical property testing could be greatly simplified, as quick estimates of the strength and elastic constants of an unknown sandstone could be predicated on the basis of one or two simple measurements. A set of 150 like samples has been selected and prepared in the Franklin laboratory for tests to determine the effects of interstitial water and oil on the physical constants of the rock.

In an effort to obtain a more efficient method of cleaning out old producing wells in the Appalachian area, an experiment was made by engineers of the Bureau of Mines Franklin office to test the idea that filling the space in the well bore around the explosive charge with gelled kerosine, a semirigid gel, and completely confining the shot with solid stemming, would cause the pressure resulting from the explosion to reach and to be maintained at a higher level for a longer period of time than if a liquid such as oil or water surrounded the charge. The creation of higher pressures by the explosion was considered desirable in order to increase the strain generated in the rock by the explosion. If the semirigid gel would slow dissipation of the well-bore pressure after the explosion by virtue of the fact that gels will not enter the small pores of the sand face as readily as do liquids, it was expected that the reisdual well-bore pressure might be high enough to hydraulically extend the fractures created by the strain waves from the explosion. An additional effect hoped for was that the transfer of the heat generated by the explosion to the gelled kerosine would raise its temperature enough to melt and take into solution the paraffin on the sand face, thus aiding in cleaning the well face.

This experiment was made on a West Virginia well in cooperation with the South Penn Natural Gas Co., the Halliburton Oil-Well Cementing Co., Stanolind Oil & Gas Co., and James M. Bird, Electric Well Surveys. The increase obtained in oil-production rates of the well were not as large as were estimated to result from conventional shooting practice. However, the cement stemming did not provide complete confinement of the explosion; and this, with other evidence, indicates the desirability of a second field test.

21/ Atchison, Thomas C., Jr., Grant, Bruce F., and Duvall, Wilbur I., Progress Report on Well-Shooting Research: Presented before the Spring Meeting of the Eastern District Am. Petrol. Inst. Division of Production, Pittsburgh, Pa., Apr. 4, 1952, paper 826-23-G.

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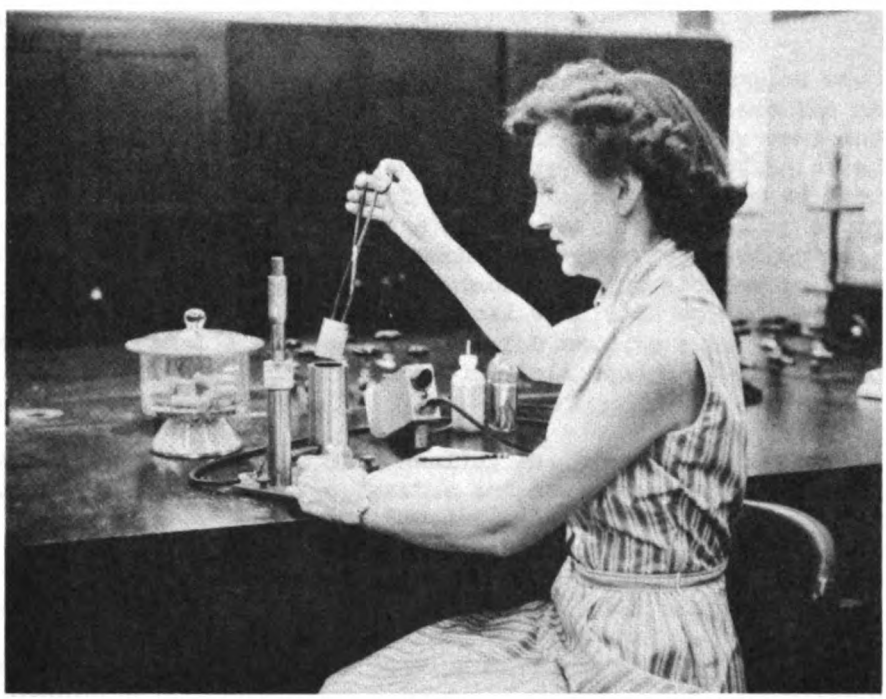

Figure 6. - Apparatus to measure bulk volume of core samples.

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Laboratory Studies

Core and Water Laboratories

The core and water laboratories at Bartlesville completed two major projects begun during the preceding year. This work included determination of porosity, permeability, and connate-water content of a large number of cores in connection with the petroleum-engineering study of the Scurry Reef field, Tex., and complete mineral analyses and resistivity measurements on more than 550 samples of brines from Kansas oil fields for use in a survey of formation brines in Kansas. Numerous miscellaneous analyses were made in connection with other petroleum-engineering and research problems.

Routine core analyses completed during the year included 1,514 permeability measurements, 1,491 porosity measurements, 1,169 determinations of connate-water content by the evaporation method, and 32 by the restored-state method. Two hundred-forty brine analyses were completed.

An apparatus (fig. 6) to measure bulk volumes of core samples was designed, constructed, tested, and placed in operation. Developed to replace the mercury pycnometer used earlier in the laboratory, the new apparatus combines ease and speed of operation with a high degree of accuracy. The apparatus consists of a U-shaped cell partly filled with mercury and an electronic contact-indicating device. The cell is designed so that the rise in the surface of the mercury caused by submerging a test specimen in it may be measured on an attached micrometer. The contact indicator produced an electrical signal when a probe attached to the micrometer screw touches the surface of the mercury. Bulk volumes measured with this apparatus have a precision of ± 0.2 percent on samples having a volume of 5 cc., to ± 0.05 percent on samples having a volume of 60 cc. A paper describing this equipment is being prepared for publication.

The core-testing facilities at Franklin, Pa., were expanded during the year. A new gas- and liquid-permeability apparatus and new gas-expansion porosimeters were fabricated. Equipment was purchased for determining the minimum interstitial water content of small core samples, which was installed in the laboratory. The porosimeters, bulk volumeters, and permeability apparatus were designed to test NX (2-1/4-inch diameter) diamond-drill cores as well as the small samples ordinarily used. The NX core-testing equipment was installed so that samples of NX size could be prepared for physical-property (sonic) testing of the same rock specimens at the College Park, Md., Station.

The equipment for determining the minimum interstitial water contents of small core samples by their desaturation through a semipermeable membrane (so-called restored-state test) is being operated to test the samples obtained several years ago from coring seven Appalachian formations with oil-base mud. Comparison of the core analysis and restored-state water content data will provide a basis for using the latter technique to evaluate the water content of other reservoirs from cores cut with water.

Effect of Brine Solutions on Permeability

A knowledge of the physical properties of the reservoir rock is necessary to determine the susceptibility of the reservoir to secondary-recovery processes and to evaluate a depleted oil field as a secondary-recovery prospect. Results of studies showed that, in the case of the Frontier formation in the Big Horn Basin, Wyo.:22/

22/ Baptist, O. C., Smith, W. R., Cordiner, F. S., and Sweeney, S. A., Physical Properties of Sands in the Frontier Formation, Big Horn Basin, Wyo.: Wyo. Geol. Assoc. Guidebook, Seventh Annual Field Conference, 1952, pp. 67-73.

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(1) The sands are permeable to waters containing sodium chloride; however, as the salt concentration is decreased, the permeability likewise is decreased; (2) exposure of the sands to fresh water will cause almost complete plugging; (3) the permeability of the core samples to dry air probably is much higher than the actual reservoir permeability; (4) natural water drive in the Frontier sands is found to be generally ineffective and may be attributed in part to the decrease in permeability of the sands when exposed to fresher waters because as the original strong brines in the sands were diluted by percolating meteoric waters, the effective permeability of the sand was decreased. Conclusions such as these were based upon the laboratory determination of the following physical properties of the Frontier sands: Oil saturation, water saturation, porosity, amount of clay, type of clay, water saturations at various capillary pressures, permeability to air and to various brines, oil recovery by water drive, and oil recovery by gas drive.

An important concept relative to the flow of liquids through porous mediums under certain conditions was developed. Results of flow tests in a radial manner through core samples disclosed that D'Arcy's equation is not applicable at low pressure differentials when the outflow face of the sample is exposed to the atmosphere. If these conditions pertain, appreciable errors in the determination of radial permeability will result.

Recovery Efficiency of Water-Flooding High-Viscosity Oils

Laboratory experiments to determine the relation between oil viscosity and recoverability by water flooding were continued in the San Francisco laboratory. One complete series of experiments, covering the range of oil viscosities from 1 to 850 centipoises (dynes per sq. cm. x 0.01) has been completed, and a second series is being run using improved apparatus and experimental technique. Preliminary results have indicated that a smaller percentage of high-viscosity oil was recovered from the core by water flooding than was recovered when the core contained a low-viscosity oil. It is significant, however, that with very viscous oils as much as 27 percent of the oil in place has been flooded out of the core. Further work is to be directed toward the effect of varying the rate of flooding, as well as the viscosity ratio of water to oil.

Research laboratory apparatus was designed and constructed to determine such fundamental properties of the reservoir rock as the wettability of the oil sands, as measured by capillary-pressure curves, the permeabilities to oil and water, and the pore geometry of sands.

In addition, a battery of flood pots has been constructed and assembled to study the effect on recovery of oil from unextracted cores from California fields by adding surface-active chemicals to the flooding water. Comparative recoveries of oils of various viscosities will be obtained by flooding with and without such chemicals in the flood water. The cores will be flooded radially toward the central bore to minimize the end effect. Attention will be given to the nonionic type of surfactant to minimize loss of chemical by adsorption and thus make the projected use of chemicals more attractive economically.

Correlation of Residual Saturation, After Laboratory Air-Drive Tests, with Pore Patterns of Sandstones

The study of the relationships between residual-liquid (oil and water) saturation, after partial displacement of liquid by the gas-drive method in tests performed in the laboratory, and parameters of consolidated sandstone, including permeability, pore-size distribution, specific surface area, and tortuosity or pore-orientation

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factor, resulted in a progress report[23] presented at the Fifteenth Technical Conference on Petroleum Production held at the Pennsylvania State College. Each gas-drive oil-recovery test was carried to a produced gas-oil ratio equivalent to 17,000 cubic feet of gas per barrel of oil. Residual-liquid saturations of the sandstone specimens ranged from 0.516 to 0.681 of their pore volumes.

The lower residual-liquid saturations were obtained with test specimens of oil-producing sandstones having: (1) The higher permeabilities; (2) the larger-size pores; (3) the least pore surface area per unit pore volume; and (4) the least tortuous effective-flow-path length. The four parameters were evaluated for each of the test specimens by analytical procedures of the determinations of fluid flow, electrical resistivity, and those made by microscopy. Mathematical relationships between oil-recovery and sandstone characteristics were derived.

Gravitational Drainage of Oil from Unconsolidated Sands

The investigation of gravity drainage of oil from unconsolidated sands was completed and a report[24] was prepared on the effect of such factors as the viscosity of the oil, interstitial water, sand thickness and grain size on the drainage of oil from sand-packed columns. Data also are presented on the effect of heat on gravity drainage.

The results show that drainage varies inversely with the viscosity of the oil and the quantity of interstitial water in the sand. Drainage is more effective from thick sands than from thin sands and the finer the sand grains, the less the recovery of oil. For heat to be effective in sand containing low-A.P.I.-gravity oils, the oil saturation must be high and the sand body must be heated uniformly. Heat was not effective in increasing recovery of light-gravity crude oils as most of the oil drained so thoroughly by gravity that the remaining oil was not readily freed by heat. The report includes data on 10 fields in which thick or steeply dipping formations of high permeability and low interstitial water content have produced large volumes of oil by gravity drainage.

Corrosion of Metals by Dissolved Gases in Water

Corrosion is a problem in most oil fields, but it is particularly serious where water flooding is in progress because of the large amount of water to which much metal equipment is exposed. The concentrations of salts dissolved in these waters vary greatly, but it has been found that the dissolved gases are more responsible for the corrosive nature of the waters than are the salts. The quantitative corrosive effect of each of the common acidic gases (carbon dioxide and hydrogen sulfide) and of oxygen is not known. To obtain a better knowledge of these factors a series of tests is being conducted under controlled conditions to determine the corrosive effect of each gas singly and in combination with the other gases over a wide range of concentrations.

Laboratory tests to determine the corrosivity of the dissolved gases to metal in water were continued. Curves have been plotted from the data obtained showing graphically the corrosion caused by different concentrations of free carbon dioxide

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23/ Tignor, E. M., Noonan, John F., and Lockwood, William N., Pore Studies of Petroleum-Reservoir Sandstones: Pennsylvania State College, Mineral Industries Experiment Station, Bull. 59, 1951, pp. 128-138; Producers Monthly, vol. 16, No. 7, May 1952, pp. 16-23.

24/ Higgins, R. V., Laboratory Studies of Factors Influencing Gravity Drainage of Oil from Sand-Packed Columns. To be published in trade press.

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with the concentration of dissolved oxygen maintained constant, and of different concentrations of oxygen with the concentration of free carbon dioxide maintained constant. Tests now are being conducted with hydrogen sulfide in varying concentrations as the corroding medium.

The results obtained to date indicate that the magnitude of corrosion caused by free carbon dioxide in water is greater than generally is recognized. In comparable concentrations, as is generally recognized, oxygen is more corrosive than carbon dioxide. However, with high concentrations of carbon dioxide, comparable to those encountered in actual tests (100 to 400 p.p.m.), carbon dioxide may cause more severe corrosion than oxygen at the maximum concentration resulting from solution of air (approximately 9 p.p.m.). The corrosion from either gas increases disproportionately when the other gas is present. In tests run to date with hydrogen sulfide as the corroding medium, the curve plotted from the data obtained tends to flatten above a critical concentration (about 125 p.p.m.), indicating that, above that point, corrosion may be essentially constant.

Figure 7 is a composite photograph showing both sides of the rack on which the laboratory dissolved-gas corrosion apparatus is mounted.

Tracers in Waters Used for Subsurface Injection

The use of data obtained with subsurface instruments, from core analyses, and from geological information permits calculation of theoretical subsurface flow patterns and rates. These calculations apply to practice only if the formation through which the water moves is homogeneous both horizontally and vertically. It is well-known that such homogeneities rarely, if ever, exist in petroleum reservoirs. Consequently, a tracer that may be added to injection water at input wells and detected qualitatively or, preferably, quantitatively at producing wells is of utmost importance in determining subsurface flow patterns and rates. This tool would provide information that would make possible remedial measures, such as selective plugging, thereby permitting more efficient oil recovery.

A radioactive tracer appears to be particularly suitable for this purpose, but unfortunately most materials that appear useful as tracers in most respects are readily adsorbed by the oil sand and therefore would not reach the producing wells.

Numerous substances have been tested to determine the extent of their adsorption on natural sandstone surfaces. Of the materials tested two, iodine and hydrogen, appear to offer possibilities as tracers in their radioactive forms. Iodine would be used as an iodide, tagged with iodine 131, and tritium (hydrogen 3) would be used to replace one of the atoms in the water molecule.

Iodine 131 has a hard gamma radiation (0.64 Mev maximum) and a half-life of 8.0 days. Detection would be comparatively easy, but this tracer could be used only in areas of high permeability or where bypassing or channeling was occurring, permitting passage of the water from input to producing wells in three to five half-lives (24 to 40 days). One advantage of the hard gamma radiation is that it is detectable in well bores with subsurface instruments.

Tritium has an extremely soft beta radiation (0.02 Mev) and a half-life of 12.5 years. The detection and counting of tritium, therefore, requires special techniques and equipment. A tritium-counting apparatus, utilizing an external high-voltage supply and quench circuit, has been constructed and is being tested for sensitivity and accuracy.

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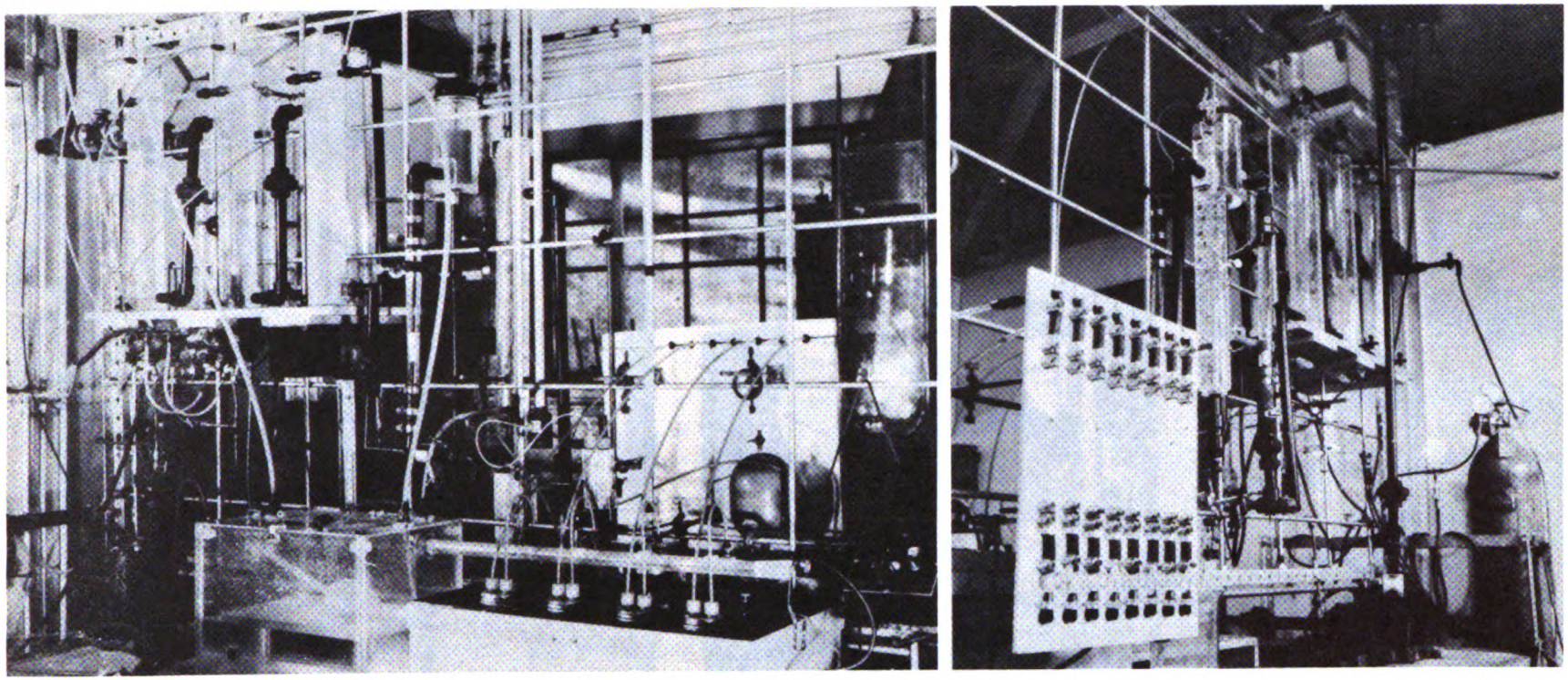

Figure 7. - Composite photograph of laboratory dissolved-gas corrosion apparatus.

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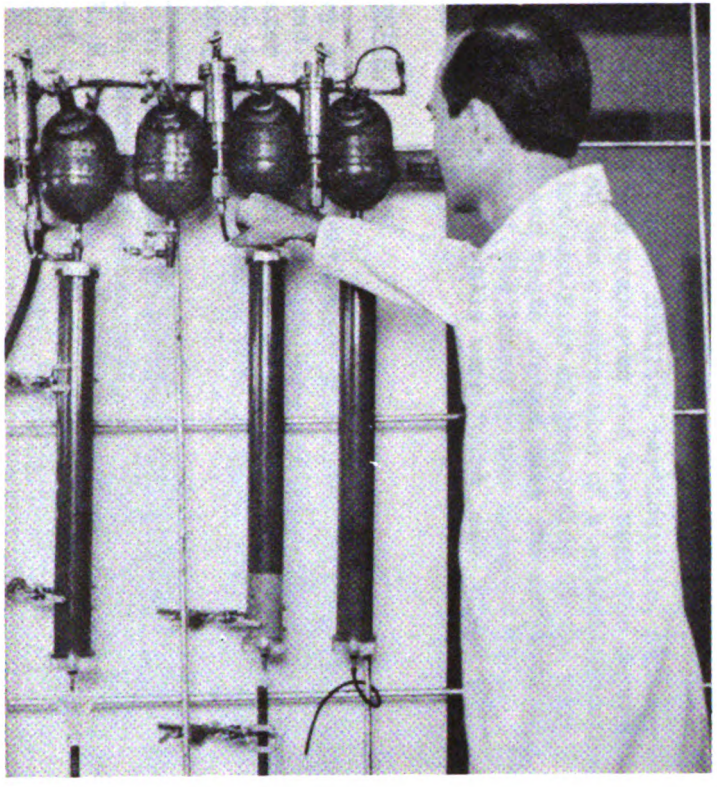

Figure 8. - Laboratory water-tracer adsorption apparatus, showing test in progress.

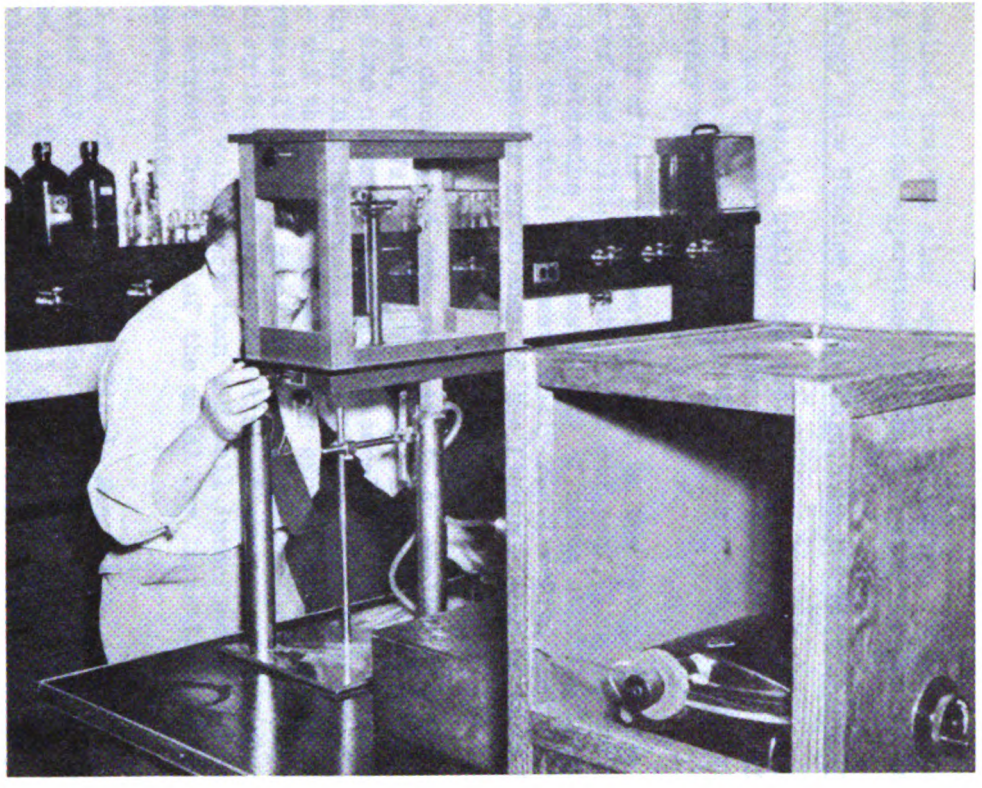

Figure 9. - Physical-properties laboratory, showing refractometer in foreground and density determination being made on specific-gravity balance.

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Other possible tracers also are being evaluated. Figure 8 is a photograph of the laboratory adsorption apparatus showing a tracer throughput test in progress.

Electrical Analogy Flow Studies of Gas Injection and Water Flooding

An electrolytic model utilizing the analogy established between Ohm's law of electrical flow and D'Arcy's law of fluid flow through porous mediums has been used in the laboratory at Franklin, Pa., to study the advance of injected fluids in secondary oil-recovery projects.

A model study of the pilot water flood in the Second Venango sand in the Nectarine area of the Bullion-Clintonville oil pool, Venango and Butler Counties, Pa., was made to determine the feasibility of using existing irregular well patterns or drilling wells to obtain a geometrically regular five-spot pattern. The model indicated the volumetric efficiency of the floods within the two five-spot patterns would be the same.

Attempts to check field data relative to an earlier (1949) helium-tracer study in the Cabin Creek, W. Va., field[25] on the electrolytic model proved that the model will check the time of arrival of the tracer-laden gas in the first-line offset producing wells to an injection well, but will not check time of arrival of injected gas in second- and third-line offset wells except in the ideal case of uniform thickness, permeability, and porosity. In the Cabin Creek field tests the effective permeability distribution affected the time of arrival of injected gas in second- and third-line offset wells more than did well interference. This conclusion, however, does not detract from use of the model for investigating sweep efficiencies of well-pattern arrangements.

The model study of the Brenneman Field, Hancock County, W. Va.,[26] earlier reported, indicated why the gas-injection operations in this field were so successful. It is estimated that the volume of oil gained (357,000 barrels) by gas injection would be equivalent to 105 barrels per acre-foot. The model indicated that of the 22.8 percent of the total field studied, 94.7 percent would be affected by the injected gases.

At the Petroleum Experiment Station, Bartlesville, Okla., the electrolytic section of the flow analyzer was completed and was used for several preliminary runs. Also, some work was done on the construction of a potentiometric flow analyzer. A study was made with the flow analyzer of properties in the West Colony field in Anderson County, Kans. These tests showed that the existing well pattern does not provide an efficient sweep of the lease by the injected fluid. Through trial the best locations for additional wells were found, and it was concluded that one existing well should be closed in.

Electrical Logging

Laboratory studies indicate that data obtained with the shielded monoelectrode system when used in conjunction with core analysis can be interpreted quantitatively in terms of water saturation. Electrical logs of model wells made up of relatively clean isotropic sandstone specimens have yielded determined water-saturation values accurate within ± 10 percent.

25/ Frost, E. M., Jr., Helium Tracer-Gas Studies in the Cabin Creek, W. Va., Oil and Gas Field: Bureau of Mines Rept. of Investigations 4715, 1950, 28 pp.

26/ Tignor, E. M., Nabors, W. M., Jennings, Thomas, and Krause, Leon, Secondary Recovery of Oil by Air and Gas Injection in the Brenneman Field, Hancock County, W. Va.: Bureau of Mines Rept. of Investigations 4690, 1950, 26 pp.

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Design and fabrication of a shielded monoelectrode system applicable to field use is in progress. The field logging equipment will consist of an hydraulic system powered by a four-cylinder gasoline engine, a cable reel, 4,000 feet of four-conductor neoprene-insulated electrical cable, a 60 volt d. c. voltage supply, a four-foot electrode, and the necessary instrumentation.

Retention of Petroleum by Reservoir Rock

The longe-range research program concerned primarily with surface forces in petroleum reservoirs has been extended to include studies of the physicochemical relationships between surface forces and surface-active substances indigenous to petroleum reservoirs or introduced into the formation. The program is designed to link academic research with industrial-production research. Therefore, it is broad in scope and extends from entirely theoretical treatments to practical applications of established principles.

Fluid-Flow Phenomena

The initial phase of liquid permeability studies of several quartz-powder samples has been essentially completed. For dimensionally stable and chemically inert systems, permeation follows the classical Kozeny-Carman equation when the porosity of the packed bed is uniform enough to result in liquid flow over the entire particle surface. Such porosity conditions were attained when the powder was dispersed by the permeating liquid.27/

It has been theoretically demonstrated that all electrokinetic processes in a porous solid can be described by two equations containing four variables: Current, flow, pressure, and voltage. This treatment required the use of three parameters: (1) Electrical conductance; (2) permeability; and (3) electropermeability.28/ These equations were tested by electrokinetic studies of the quartz-acetone system. It was found that the electroviscous effect was little larger than the experimental uncertainty in measuring permeability. These experiments indicate that electrokinetic effects in nonaqueous liquids probably are caused by foreign ions from the solid.29/

Detergents in Water-Flooding Operations

Studies to determine the conditions required to make use of a general type of detergent economically feasible for oil-recovery operations have begun. Simplified, rapid experimental methods for these studies have been established. When the data from such experiments are interpreted according to modern theories of chromatography, the following properties of a detergent may be established.

1. The amount of detergent removed from solution by contact with various surfaces and the reversibility of this process.
2. The rate of detergent movement through a formation relative to the water-flood movement.
3. The effectiveness of a detergent in wetting reservoir materials.

27/ Johansen, R. T., Lorenz, P. G., Dodd, C. G., Pidgeon, F. D., and Davis, J. W., The Permeation of Water and Iso-octane Through Plugs of Microscopic Particles of Crushed Quartz: Pres. 26th Nat. Colloid Symposium, Los Angeles, Calif., June 16, 1952.

28/ Lorenz, P. B., Electrokinetic Relations in the Quartz-Acetone System: Pres. 121st meeting Am. Chem. Soc., Buffalo, N. Y., Mar. 27, 1952.

29/ Lorenz, P. B., The Phenomenology of Streaming Potential and Electro-osmosis: Jour. Phys. and Coll. Chem., vol. 56, No. 6, June 1952, p. 775.

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A precision surface-tension balance and thermostat have been assembled to use in the detergency studies. This research program has been coordinated with similar research programs of several oil companies and detergent producers to yield a maximum amount of pertinent information.

Reservoir Materials

An improved method for microscopic measurement of surface areas of powders has been developed.30/ This method has been used to measure the surface areas of the powders used in studies of permeability and of detergents and the surface areas of several local sands.

A color test for the qualitative identification of clay-mineral groups that may be present in petroleum reservoirs has been developed.31/

Surface-Active and Film-Forming Constituents of Petroleum

A fundamental study of the interfacial activity and film-formation of a typical porphyrin (a blood derivative) and its vanadium complex has been undertaken. The greater activity of the vanadium complex has been correlated with the changes in the hydrophobic-hydrophilic balance of the molecule caused by introducing the metal. The results of these experiments and techniques developed in their prosecution have been applied to studies of porphyrins that have been isolated from California and Oklahoma crude oils. Water-spray extraction and deasphalting methods have been used to obtain surface-active extracts from petroleum. These extracts have been studied by extensive chromatographic procedures. The surface activity, film formation, and metallic content of these extracts have been correlated in an attempt to reveal the nature of surface-active and film-forming substances indigenous to petroleum and the effect that such substances may have on various methods for the recovery of petroleum.32/

Recovery of Hydrocarbons from Bituminous Sandstones

Publication of the results of separation and utilization studies of oils from sandstones of the Vernal and Sunnyside, Utah, deposits33/ completed the Bureau's long-term study of methods of obtaining hydrocarbons from the large outcropping deposits of oil-soaked sandstones in the United States.

Part I of this report summarizes the general characteristics of the Vernal and Sunnyside deposits and discusses the hot-water separation process as applied to these sandstones and the results obtained. The separation tests showed that these sandstones respond to treatment by the hot-water method of separation.

30/ Pidgeon, F. D., and Dodd, C. G., Improved Procedure for Precise Particle Surface Area Measurement with the Microscope: Pres. 12th Internat. Cong. Pure and Applied Chem., New York, N. Y., Sept. 13, 1951.

31/ Hambleton, W. W., and Dodd, C. G., A Qualitative Color Test for the Rapid Identification of the Clay Mineral Groups: Pres. 120th meeting Am. Chem. Soc., New York, N. Y., Sept. 6, 1951.

32/ Dodd, C. G., Moore, J. W., and Denekas, M. O., Metalliferous Substances Adsorbed at Crude Petroleum-Water Interfaces: Ind. Eng. Chem., vol. 44, No. 11, 1952, pp. 2632-2635.

33/ Shea, G. B., and Higgins, R. V., Wenger, W. J., Hubbard, R. L., and Whisman, M. L., Separation and Utilization Studies of Bitumens from Bituminous Sandstones of the Vernal and Sunnyside, Utah, Deposits. Part I. Laboratory Hot-Water Separation Tests. Part II. Analytical Data on Asphalt Properties and Cracked Products of the Separated Bitumens, Bureau of Mines Rept. of Investigations 4871, 1952, 28 pp.

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Part II of the report presents analytical data that indicate possible uses for the products. The method of utilizing the extracted oil depends upon the amount of processing that can be done profitably. If only a minimum amount of processing is allowable, the high molecular weight of the oils makes it necessary to consider their use as fuel oils or as asphalts. If quality products, such as motor fuels, are desired, a coking-distillation process might be used in which the oil is distilled under ordinary pressures and at cracking temperatures until only a residue of dry coke remains.

PETROLEUM CHEMISTRY AND REFINING

For several years research on the chemistry and refining of petroleum has been directed toward learning more about relationships between the composition of petroleum and utilization of petroleum products. The program has been maintained flexible so that different phases might be emphasized as dictated by changing conditions in the refining industry. For example, during the present year current refinery runs of high-sulfur crude oils and increased interest in the composition and combustion characteristics of Diesel fuels resulted in increased emphasis on these parts of the program.

The different parts of the program are closely related, but for purposes of discussion they can be divided conveniently into the following six headings:

1. Characteristics and Availability of Crude Oils and Products.
2. Separation and Identification of Sulfur Compounds in Petroleum.
3. Chemical Studies of Fuels.
4. Combustion Research on Fuels.
5. Composition and Properties of Asphalt.
6. Fuel Surveys.

Characteristics and Availability of Crude Oils and Products

During the year 145 crude-oil samples from domestic fields and 17 samples from 14 foreign fields were analyzed by the Bureau of Mines routine method. Geographical distribution of the samples was as follows:

Alaska 6, Arkansas 1, California 1,
Colorado 27, Nebraska 22, Montana 3, Texas 45, Oklahoma 8,
Wyoming 32, Australia 1,
Canada 5, Germany 4, Venezuela 7.

Several reports concerning crude-oil analyses are in preparation. Included among these is an additional tabulation of West Texas analyses.34/ This report will give 100 analyses of crude oils from the West Texas area analyzed during the past 6 years. The paper includes subdivisions for the Scurry County Reef and Spraberry Trend crude oil analyses.

Parts 5, 6, and 7 of a series of reports regarding refining characteristics of recently discovered crude oils were prepared. The first of these reports discussed

34/ Garton, E. L., and McKinney, C. M., Analyses of Crude Oils from Some West Texas Fields: II. Additional Analyses, Bureau of Mines Rept. of Investigations 4959, 1953.

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analyses of crude oils from the "Golden Trend" in Oklahoma,35/ the second examined analyses of crude oils from the Julesburg Basin,36/ and the third report discussed analyses of crude oils from the recently discovered fields in Alberta, Canada.37/

A statistical study of 330 crude oils, representing 65 percent of all the crude oil produced in the United States, was published in the Proceedings of the Third World Petroleum Congress.38/ The following properties were shown by bar graphs: Sulfur content, viscosity, asphalt content, naphtha and gas-oil content, percentage of aromatics in the naphtha and gas oil, percentage of aromatics and paraffins-plus naphthenes in the naphthas and gas oils, and proportion of naphthene ring and paraffinic chains in the paraffin-naphthene portion.

The wide coverage of crude oils that have been analyzed by the Bureau of Mines routine method enhances its value to the petroleum refiner. This was emphasized at a recent meeting where the procedure and its significance were discussed.39/ Refinery representatives asked questions regarding the procedure and also suggested ways in which it could be amplified to overcome some of its deficiencies.

A survey of nitrogen contents of crude oils from various sections of the United States was published.40/ Analyses of 153 crude oils were reported and correlations were developed between nitrogen content, carbon residue of the crude oil, and the geological formation from which it was produced. These enabled estimations of nitrogen content to be made from data contained in Bureau of Mines routine crude-oil analyses.

Sulfur Compounds in Petroleum

Work under American Petroleum Institute Research Project 48A on the Production, Isolation, and Purification of Sulfur Compounds and Measurement of their Properties has continued. As in past years this research is separated into three independent but related phases, which are:

1. Synthesis, purification, and determination of properties of sulfur compounds;
2. Separation, isolation, and identification of sulfur compounds in crude oils; and
3. Determination of thermodynamic data of sulfur compounds.

35/ Smith, N. A. C., Smith, H. M., and McKinney, C. M., Refining Properties of New Crudes. Part 5 - Characteristics of Crude Oils from the "Golden Trend" in Oklahoma: Petrol. Processing, vol. 6, No. 9, September 1951, pp. 987-990.

36/ Wenger, W. J., and Ball, J. S., Refining Properties of New Crudes. Part 6 - Crude Oils from the Julesburg Basin, Colorado, Nebraska, and Wyoming: Petrol. Processing, vol. 7, No. 6, June 1952, pp. 821-825.

37/ McKinney, C. M., and Smith, H. M., Refining Properties of New Crudes. Part 7 - Crude Oils from Recent Discoveries in Canada: Petrol. Processing, vol. 7, No. 9, September 1952, pp. 1270-1273.

38/ Smith, H. M., Composition of United States and Some Foreign Crude Oils: Proc. Third World Petrol. Cong., Section VI. Leiden, Netherlands, 1951, pp. 319-335.

39/ McKinney, C. M., Significance and Interpretation of the Bureau of Mines Routine Crude Oil Analysis: Pres. Western Petroleum Refiners Association Regional Meeting, Beaumont, Tex., Feb. 8, 1952.

40/ Ball, John S., Whisman, M. L., and Wenger, W. J., Nitrogen Content of Crude Petroleums: Ind. Eng. Chem., vol. 43, 1951, pp. 2577-2581.

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The first two phases of this project are being carried out at Laramie, Wyo., and Bartlesville, Okla., respectively, and are discussed below. The third phase is conducted at Bartlesville and is discussed under the section on Thermodynamics of Petroleum in this report.

Synthesis, Purification, and Determination of Properties of Sulfur Compounds

The scarcity of reliable data on the physical properties of sulfur compounds has prompted establishment of a program on the purification and determination of physical properties of sulfur compounds. This work, which is done in cooperation with the American Petroleum Institute as part of API Research Project 48, has as its chief purpose development of information that can be used in devising analytical methods for the sulfur compounds of petroleum and its products.

During the past year 6 sulfur compounds have been purified, in addition to the 15 from previous years, making a total of 21. The six for this year are: 2-methylthiophene, thiacyclohexane (pentamethylene sulfide), 2-thiapentane (methyl n-propyl sulfide), 2-butanethiol (sec-butyl mercaptan), 3-methyl-2-thiabutane (methyl isopropyl sulfide), and 4-thiaheptane (di-n-propyl sulfide). All of the compounds in this program are purified to a purity of 99.9 mole percent or better, as determined by a freezing-point purity determination.

Precise measurements of freezing point, boiling point, refractive index, density, surface tension, and viscosity are to be made on each of these sulfur compounds and have been completed on the first 15 compounds. Figure 9 shows a portion of the laboratory in which these determinations are made. Ultraviolet, infrared, and mass spectra are obtained and reported to A.P.I. Research Project 44 for publication in its catalogs of spectral data. Thus far, 15 ultraviolet spectra, 15 infrared spectra in the 2-15 micron wave-length range, 20 infrared spectra in the 15-25 micron wavelength range, and 11 mass spectra have been completed.

The project also acts as a clearing house in obtaining spectra of other sulfur compounds. Donations of sulfur compounds even through they are not of high purity have been accepted. When the amount is large enough, some purification and an estimate of purity are made. The samples are then sent to cooperating petroleum industry laboratories for determination of spectra. Since the clearing house program was begun in August 1949, 56 samples have been donated, 18 compounds have undergone purification, and 124 spectra of various types (ultraviolet, infrared, Raman, and mass) have been returned from the 10 cooperating laboratories.

The availability of many hitherto unprocurable sulfur compounds makes it possible to reevaluate techniques for analyzing sulfur compounds. A method published by the Bureau of Mines[41] and used extensively in the petroleum industry is being tested through its use on synthetic samples containing known sulfur compounds. A paper has been prepared[42] and a discussion included concerning the use of spectra and physical property data in the analysis of petroleum fractions.

The samples of purified compounds besides their use for the determination of physical properties, are used in other phases of A.P.I. Project 48 for determination

41/ Ball, John S., Determination of Types of Sulfur Compounds in Petroleum Distillates: Bureau of Mines Rept. of Investigations 3591, 1941, 60 pp.

42/ Haines, W. E., Helm, R. V., Bailey, C. W., and Ball, John S., Purification and Properties of Ten Sulfur Compounds: Preprints, General Papers Presented Before the Division of Petroleum Chemistry of the American Chemical Society, No. 28, September 14-19, 1952, pp. 119-133.

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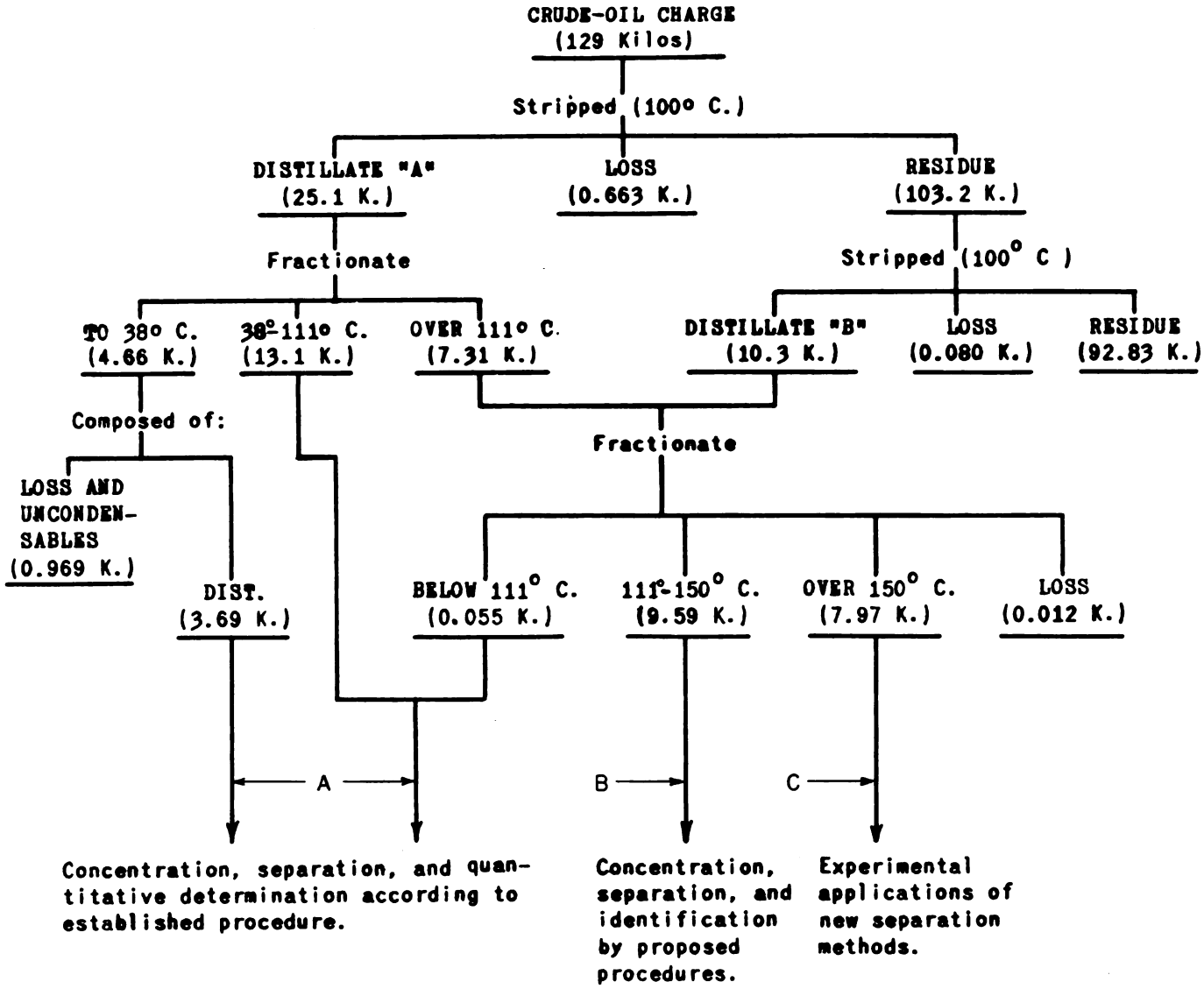

Figure 10. - Systematic separation of sulfur compounds.

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of thermodynamic properties and for standards in the isolation of sulfur compounds from petroleum. A portion of each purified compound is bottled into 5-ml. ampoules and sold by the American Petroleum Institute as calibration standards to use with spectrometers in industry laboratories. Samples of purified compounds also are given to qualified investigators for research in specialized fields. In this latter category, some 30 samples have been sent to various laboratories for investigation of such widely-divergent fields as spectral determinations, analytical procedures, microbiology experiments, electron-diffraction studies, and decomposition studies.

Separation and Identification

During 1951-52 the project has continued identification of sulfur compounds in a Wasson, Tex., crude-oil distillate. The sulfur compounds in the distillate boiling below 100° C. were concentrated by selective adsorption on alumina. This concentrate was fractionated, and the sulfur compounds were identified by examining the fractions with the infrared spectrophotometer. All theoretically possible sulfur compounds boiling below 100° C. were found except carbon disulfide, thiophene, and the unstable cyclic sulfides, which probably do not occur naturally in crude oil. The compounds identified are listed in table 3, which gives their boiling points and the quantity of each estimated to be present in the original crude oil. The percentages reported are believed to be accurate to 10 to 15 percent.

TABLE 3. - Sulfur compounds identified in Wasson, Tex., crude oil and estimated weight percent present where known

Name	Boiling point, °C.	Weight percent in Wasson, Tex., crude oil
Elemental sulfur	444.6	Less than 0.001
Hydrogen sulfide	-61.8	Trace.
Methanethiol (methyl mercaptan)	6.5	0.00240
Ethanethiol (ethyl mercaptan)	35.0	.00530
2-Thiapropane (methyl sulfide)	37.4	.00008
2-Propanethiol (isopropyl mercaptan)	52.5	.00199
2-Methyl-2-propanethiol (t-butyl mercaptan)	64.2	.00055
2-Thiabutane (methyl ethylsulfide)	66.7	.00222
1-Propanethiol (n-propyl mercaptan)	67.8	.00041
2-Methyl-2-thiabutane (methyl isopropyl sulfide)	84.8	.00064
2-Butanethiol (sec-butyl mercaptan)	85.2	.00386
2-Methyl-1-propanethiol (isobutyl mercaptan)	88.7	.00003
3-Thiapentane (ethyl sulfide)	92.1	.00075
2-Thiapentane (methyl n-propyl sulfide)	95.5	.00030
1-Butanethiol (n-butyl mercaptan)	98.4	Trace.
2-Methyl-2-butanethiol (t-amyl mercaptan)	99.0	.00064
3,3-Dimethyl-2-thiabutane (methyl tert-butyl sulfide)	99.0	Not determined.
Cyclohexanethiol	158.0	Do.

To continue this identification program to higher temperatures and to verify the percentages in the lower boiling range, a larger quantity of distillate was prepared. Fifty gallons (129 kilograms) of Wasson crude oil was stripped at 100° C. in two stages, and the distillate obtained was fractionated into appropriate and definite boiling-range cuts. The procedure is outlined in figure 10. In this outline, distillate "A" will be used to substantiate with increased accuracy the data of table 3, and distillates "B" and "C" will be used to continue the identification of sulfur compounds into the higher boiling ranges.

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In the higher-boiling distillate "B" (111° to 150° C.), it will be necessary, because of the ever increasing number of sulfur compounds in each higher temperature interval, to resort to chemical methods to separate the alumina-concentrated sulfur compounds into sulfur types (such as mercaptans and sulfides) before separating individuals by fractionation and identification by infrared or chemical methods. Several separation methods based on sulfur-compound type or on the structure of the hydrocarbon portion of the molecule are now under development. These include extracting of mercaptans with sodium aminoethoxide in ethylene-diamine; separating of mercaptans into two groups containing the primary and secondary compounds in one and the tertiary in the other by forming insoluble ammonium mercaptides of the primary and secondary mercaptans in liquid ammonia; separating cyclic and chain sulfides by selective addition of the cyclic sulfides to a heavy metal salt; separating normal from branched and cyclic compounds by adducting the cyclic compounds with thiourea. Preliminary application of aminoethoxide extraction of Wasson distillate has led to the identification of cyclohexanethiol (B.P. 158° C.) and the suspected presence of 2- or 3-hexanethiol. Positive identification of the alkanethiol or thiols will follow when spectra of these compounds become available.

A polarographic method was developed for determining elemental sulfur in crude oils. The procedure was described and percentages of elemental sulfur in nine Texas crude oils were presented at a meeting of the American Chemical Society.43/ This study definitely established that elemental sulfur occurs in some crude oils, a subject that heretofore was highly controversial.

Also investigated was an amperometric method for determining the end-point of the silver nitrate-thiol titration and applying it to distillates and heavier materials, such as crude oils and their distillation residua. Although it has not been proved conclusively that the method is accurate for the heavier oils, it appears to be satisfactory in this application and yielded interesting information on the production of thiols in thermally treated crude oils.

Stability studies were continued on crude oils and on crude oils to which sulfur and polysulfides were added. Using the polarographic method to determine elemental sulfur, it was demonstrated that elemental sulfur in crude oils is the cause of (but not necessarily the sole cause) generation of hydrogen sulfide when crude oils containing this compound are heated to around 400° F. This is clearly shown in figure 11 where the elemental sulfur content of the crude-oil charge in a distillation flask drops to zero simultaneously with a rapid evolution of hydrogen sulfide. These data relate to a natural crude oil containing elemental sulfur. A synthetic blend of 0.5 percent elemental sulfur with virtually sulfur-free crude oil (Bradford, Pa.) gives identical phenomena when treated in a similar manner.

The presence or absence of polysulfides in crude oils is of considerable interest, and the behavior of these compounds during thermal treatment of crude oils therefore was investigated. Tertiary butyltrisulfide and tertiarybutylpolysulfide were added to low-sulfur Bradford, Pa., crude oil and subjected to the stability test. Results essentially similar to those with free sulfur were observed, except that there were some differences in rate of hydrogen sulfide evolution, and mercaptans were evolved also. These stability tests have commercial as well as theoretical significance as polysulfides or elemental sulfur in a crude oil, after heating to above 400° F. in commercial processes, would be expected to contain sulfur compounds not present in the original crude oil. The results of these various stability experiments are being written for publication.

43/ Eccleston, B. H., Morrison, Marilyn, and Smith, H. M., Elemental Sulfur in Crude Oil: Pres. before the Division of Petroleum Chemistry, American Chemical Society, Milwaukee, Wis., Mar. 30-Apr. 3, 1952.

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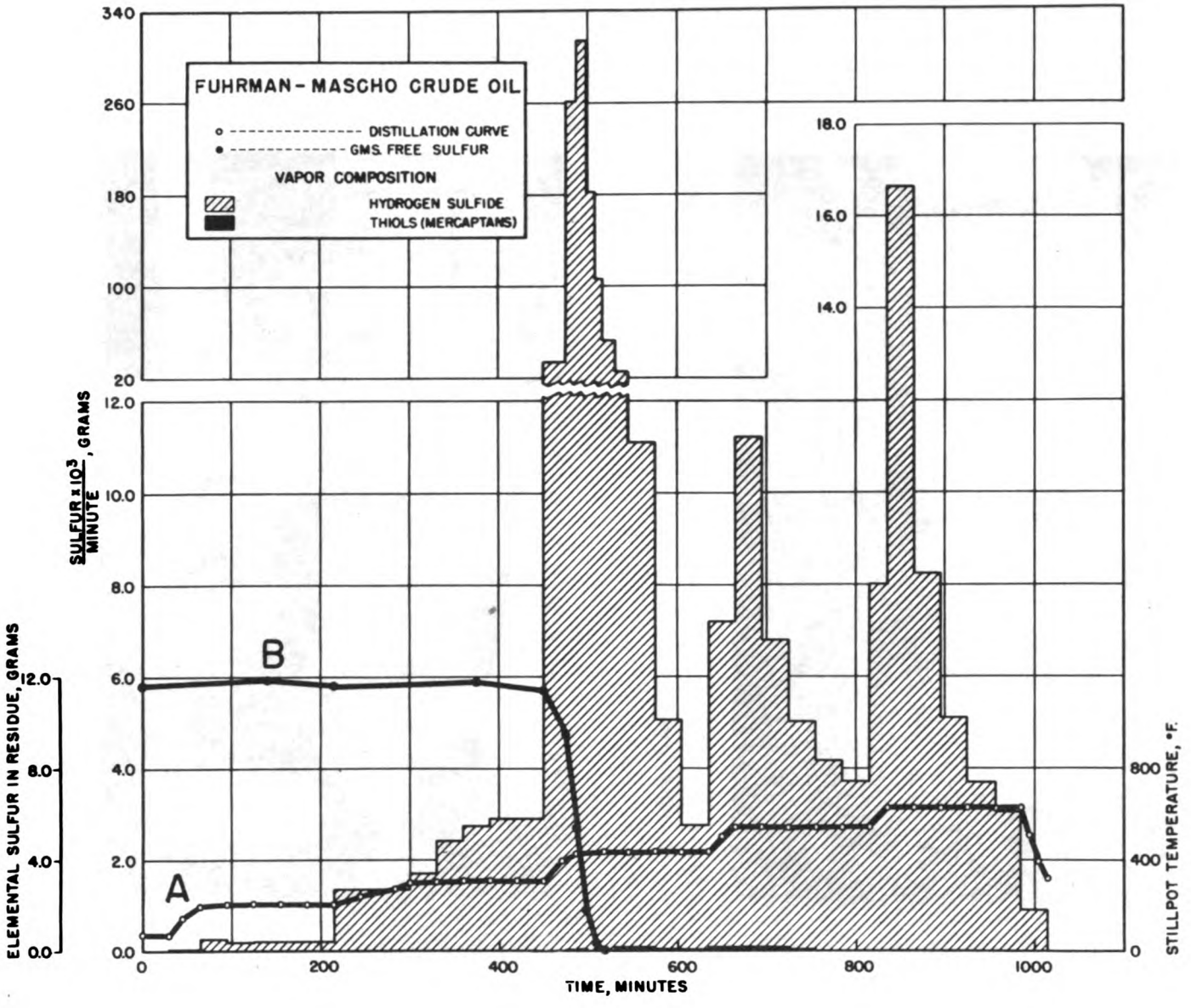

Figure 11. - Thermal-stability test of Fuhrman-Mascho crude oil.

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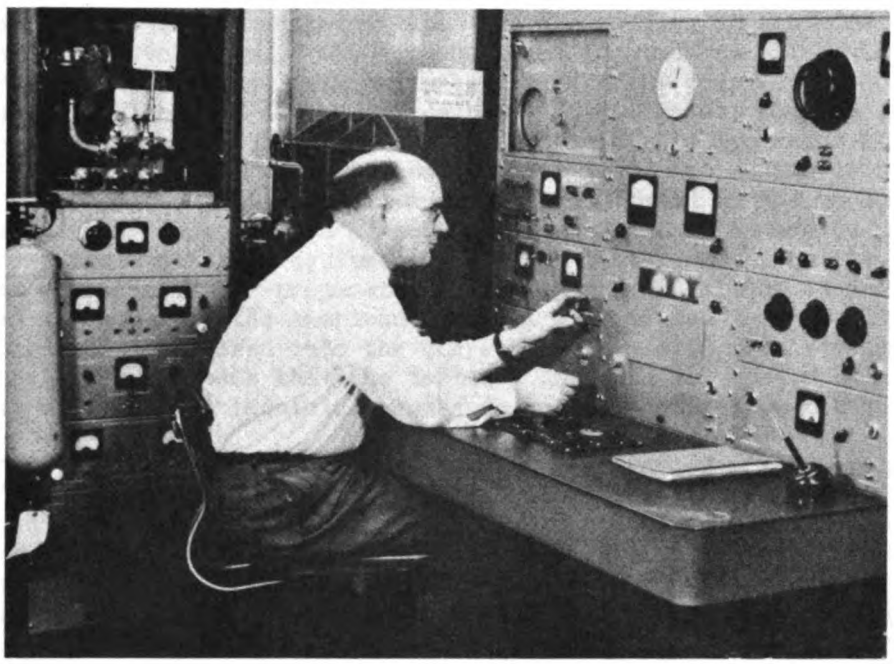

Figure 12. - Thermal decomposition products from sulfur compounds are analyzed by means of the mass spectrometer.

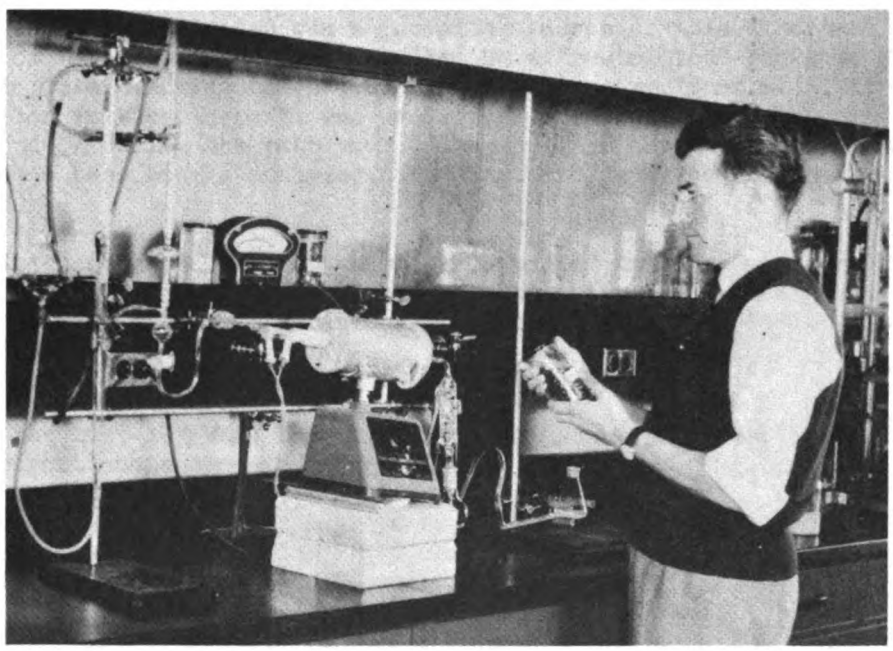

Figure 13. - Apparatus for catalytic decomposition of thiacyclopentane.

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Thermal Decomposition of Sulfur Compounds

The reactions of sulfur compounds upon the application of heat are being studied to discover the stability of the compounds and to study reactions that they may undergo in refining processes. Temperatures at which the compounds are unstable and the mechanisms by which they decompose are being investigated. One series of decompositions is carried out on pure sulfur compounds in a flow apparatus utilizing a quartz tube to minimize catalytic effects. Temperatures and residence times are varied, and the products from each run are analyzed. Based on the products formed at various stages of decomposition a mechanism for the reaction may be postulated. Figure 12 shows the analytical equipment for these tests. The first two compounds to be studied were 2-methyl-2-propanethiol and 1-pentanethiol. A description of this work was given before the American Chemical Society and later published.44/ These two compounds decomposed into the corresponding olefin and hydrogen sulfide. However the evidence suggests that the tertiary compound decomposes by a free radical reaction, whereas 1-pentanethiol breaks down essentially by a molecular splitting.

Some study has been made of the catalytic decomposition of thiacyclopentane (see fig. 13). If this compound could be dehydrogenated quantitatively to thiophene, the reaction could be used as an analytical tool. Unfortunately, using palladium catalyst at temperatures of 350°-500° C. ring cleavage is obtained yielding hydrogen sulfide as a product. Use of various catalysts and introduction of a hydrogen acceptor failed to increase the thiophene production enough to make the reaction attractive for an analytical procedure.

Chemical Studies of Fuels

Gasoline

During the period 1940-45 the Bureau prepared and analyzed aviation-gasoline base stock from crude oils representing every major field in the United States that preliminary analysis indicated was a potential source of this important product. The reports of these analyses were supplied on a "restricted" basis to petroleum refiners and to Government agencies concerned with the supply of aviation fuel. After the information in these reports was declassified the data were tabulated and they were published45/ during the past year. Chapter 1 of the report contains tabulated data on the 454 base stocks analyzed, and chapter 2 describes the equipment and procedures used.

Composition studies on the base stocks reported in this paper provided interesting data on the ratio of various hydrocarbons in crude oils. These data were presented at a meeting of the International Congress of Pure and Applied Chemistry.46/

Diesel Fuel

During the last 10 years the demand for all petroleum products has increased, with a disproportionate increase in demand for the middle distillates, which include

44/ Thompson, C. J., Meyer, R. A., and Ball, J. S., Thermal Decomposition of Sulfur Compounds. I. 2-Methyl-2-Propanethiol: Jour. Am. Chem. Soc., vol. 74, No. 13, July 5, 1952, pp. 3284-3287; II. 1-Pentanethiol. Pp. 3287-3289.

45/ Smith, H. M., Kraemer, A. J., and Thorne, H. M., Aviation Gasoline and Its Component Hydrocarbons: Wartime Research (1940-45): Bureau of Mines Bull. 497, 1951, 79 pp.

46/ Rall, H. T., and Smith, H. M., Composition of Petroleum: Relationships of Hydrocarbon Types Through C6-C9 Hydrocarbons: 12th Cong. Pure and Applied Chem., New York, N. Y., September 1951.

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Diesel fuel, jet fuel, household-burner fuel, and catalytic-cracking charge stock. A straight-run distillate is preferred for all of these products, but unfortunately the supply has not been adequate to meet the increased demands, and for some uses it has been necessary to make up the deficit by blending catalytically cracked stocks with the straight-run distillates. This blending of fuels has complicated the storage problem, as some of these fuels deteriorate under normal storage conditions. It also has been found that two fuels that have good stability when stored separately may form a sludge when mixed. In Diesel fuels this sludge clogs the engine filters and injector nozzles, causing engine failure. Recognizing this problem, the Western Petroleum Refiners Association and the Bureau of Mines on May 1, 1951, entered into a cooperative agreement to study the basic causes of the instability and incompatibility of Diesel fuels. The program was set up with two objectives: (1) To make a comprehensive laboratory study of representative distillates under a variety of storage conditions identically imposed; (2) to determine the causes of the phenomena that result in the instability and incompatibility. The program was set up to include most of the important producing areas of the United States, plus samples from Canada, Mexico, Venezuela, and the Middle East. Wherever possible, an attempt was made to obtain a straight-run fuel, a thermally cracked fuel, and a catalytically cracked fuel from the same crude-oil source. Where this was not possible a catalytically cracked fuel and a thermally cracked fuel were obtained from a crude oil in the same area. A total of 33 basic stocks was used in the storage program, and in addition approximately 60 blends were made of fuels that might be blended commercially. This made a total of between 90 and 100 stocks and blends, and all fuels were handled in the same manner in the storage program.

Vented 1-pint sample bottles were used for storing the fuels under the following conditions:

1. Sample as received.
2. Iron plus tap water.
3. Copper.
4. Copper plus sea water.
5. Iron.
6. Galvanized iron plus sea water.
7. With a distilled water wash.

Five pint bottles were stored for each condition for each of the samples and blends. Thus about 90 samples stored under 7 conditions with 5 bottles for each condition make a total of about 3,000 sample bottles in storage. These sample bottles were stored in a hot room at 110° F. For about 2 hours out of every 24 the storage-room temperature was reduced to 90° F. to promote breathing of the samples and renew the air supply in the bottles.

All of the usual inspection tests were made on the samples as received, and these will be repeated at 39 weeks, the end of the storage program. In addition, special tests were made. It is hoped that these will give some clues as to the causes for instability. Also, interim tests are being made at the end of 6 weeks, 13 weeks, and 26 weeks. These interim tests consist of visual examination, insoluble gum, soluble gum, and color.

The storage program is well under way and some work has been done toward investigating the causes of instability and incompatibility of these fuels. All of the stocks and blends are in storage, and most of the initial tests have been completed, as well as the interim 16-, 13-, and 26-week tests. From these data, some of which

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have been reported[47] to the sponsoring organization, definite patterns are beginning to form, and it is becoming clear why earlier investigations based upon a study of one fuel or one type of fuel have resulted at times in misleading conclusions that may not be applicable to other types of fuels.

The accelerated storage of fuels in contact with selected catalysts is suitable for a research program, but, from a practical point of view, it is necessary to relate these storage conditions to those that prevail at atmospheric temperature in steel drums or storage tanks. To obtain data for such a correlation, a supplementary drum-storage program was commenced. Samples of 24 of the fuels used in the laboratory-storage program were stored in vented drums at atmospheric conditions in an open shed. Alongside the drums were samples in vented one-pint glass sample bottles stored in the dark at atmospheric conditions. This will provide an opportunity to compare drum storage with vented samples in glass at atmospheric conditions and with vented samples in the 110° F. storage room.

Government authorities concerned with supplying petroleum products have indicated that, in an emergency, nonmilitary Diesel-fuel consumers would be forced to use fuels that contain a greater percentage of cracked stock, have a higher end point, and higher sulfur and nitrogen content. To anticipate this possibility the Coordinating Research Council (C.R.C.) is sponsoring some full-scale tests to determine the limitations of fuel that can be burned successfully in a railroad Diesel engine. Twelve special fuels have been made by refiners, and several railroads are cooperating by using one of these fuels exclusively in a locomotive on a regular run. The test engine is dismantled at regular intervals, and the parts are examined to determine the effect of operating with a fuel that is inferior to the regular fuel in one or more respects. The Bureau of Mines is participating in this program through a cooperative agreement with the C.R.C., whereby the Bureau will analyze each of the test fuels and its corresponding control fuel to determine if differences in composition of the two fuels can be correlated with full-scale railroad-engine performance. Physical, chemical, and combustion characteristics of each of the fuels were determined, each fuel was fractionated into 10 fractions, and the characteristics of each fraction were measured. Data on the fuels and fractions will be submitted to the C.R.C. analysis panel for comparison of engine performance and fuel analysis. The Bureau's participation in this program was possible only because comprehensive studies of composition and combustion characteristics that were made on representative fuels during the last 5 years provided information for developing correlations that would justify predictions of full-scale engine performance on the basis of a relatively simple analysis.

Separation techniques are being developed and refined concurrently with the composition studies. A recently developed technique for improving the degree of separation between type hydrocarbons in Diesel fuels by means of silica gel was presented at a regional meeting of the American Chemical Society.[48]

Nitrogen Compounds in Distillate Fuels

Formation of sludge in distillate fuels upon standing (stability) or upon mixing (incompatibility) has been attributed to the presence of nitrogen compounds. As part

47/ Smith, H. M., Status of Bureau of Mines-Western Petroleum Refiners Association Program on Stability of Distillate Fuels: West. Petrol. Refiners Assoc. Annual Meeting, San Antonio, Tex., April 1, 1952.
Ward, C. C., Status of Western Petroleum Refiners Association-Bureau of Mines Fuel Stability Researches: Report on Diesel Fuel Conference, Bureau of Mines, Bartlesville, Okla., May 8-9, 1952.

48/ Hopkins, R. L., High Dilution Technique in Adsorption Analysis of Diesel Fuels: 7th Southwest Regional Meeting, Am. Chem. Soc., Austin, Tex., Dec. 7, 1951.

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of a program to study this effect, the analysis of a number of distillate fuels for types of nitrogen compounds has been begun. Fuels undergoing storage tests for stability and incompatibility in another Bureau program were used so that correlations can be made. Thirty-three fuels have been tested for basic nitrogen and pyrrole nitrogen as well as total nitrogen. As most of the fuels have nitrogen contents below 0.01 percent, such determinations are not highly accurate. Consequently it is important to concentrate the nitrogen compounds before analysis. This is being done by adsorption on florisil, a synthetic magnesium silicate. By this means the nitrogen content of the concentrate may be increased to over 2.0 percent.

Combustion Research on Fuels

Constant-Volume Bomb

Development of the constant-volume combustion bomb is virtually complete, and during 1952 two of the bomb units were used to obtain both practical and fundamental data on the combustion of fuels with additives and in synthetic atmospheres. One of these studies was carried out in cooperation with the Coordinating Research Council, which derives its financial and technical assistance from both the automotive and petroleum industries. This investigation was concentrated on a study of the combustion characteristics of commercial fuels and the effects of ignition promoters in combustion of those fuels. In this work the determination of the influence of both fuel composition and of ignition promoters on the ignition and combustion characteristics of the fuels was emphasized. The investigations included pressure-temperature conditions, which bracket those developed in engine operation over a wide range of ambient temperature and speed and load conditions. Results of this study[49] were presented to a group of representatives of the petroleum and automotive industries.

Results of earlier investigations along these lines were published by the Society of Automotive Engineers.[50]

Some fundamental studies conducted with the bomb consisted primarily of investigations to determine the influence of inert gases and water vapor on the combustion of a commercial-type Diesel fuel under conditions of auto-ignition. These studies, made in cooperation with the Navy under contract, were made to obtain background information to use in evaluating closed cycle Diesel operation and to gain information on which performance of other nonstandard auto-ignition cycles could be postulated.

Evaporation of fuels after injection into heated inert atmospheres was studied to gain a better understanding of the manner in which fuels are prepared for the chemical reaction that follows injection into an atmosphere capable of starting auto-ignition of the fuel. Typical data obtained in tests of this nature are shown in figure 14.

A summary of the work on this problem from 1948-50 was released by the Coordinating Research Council.[51]

49/ Hurn, R. W., Effect of Ignition Accelerators in Bomb Combustion of Diesel Fuels: Report of Diesel Fuel Conference, Bureau of Mines, Bartlesville, Okla., May 8-9, 1952.

50/ Hurn, R. W., and Hughes, K. J., Combustion Characteristics of Diesel Fuels as Measured in a Constant Volume Bomb: Soc. Auto. Eng. Quart. Trans., vol. 6, No. 1, January 1952, pp. 24-35.

51/ Society of Automotive Engineers, Combustion Characteristics - Ignition Delay Bomb, 1948-50: Special Publications Department, 29 West 29th Street, New York 18, N. Y.

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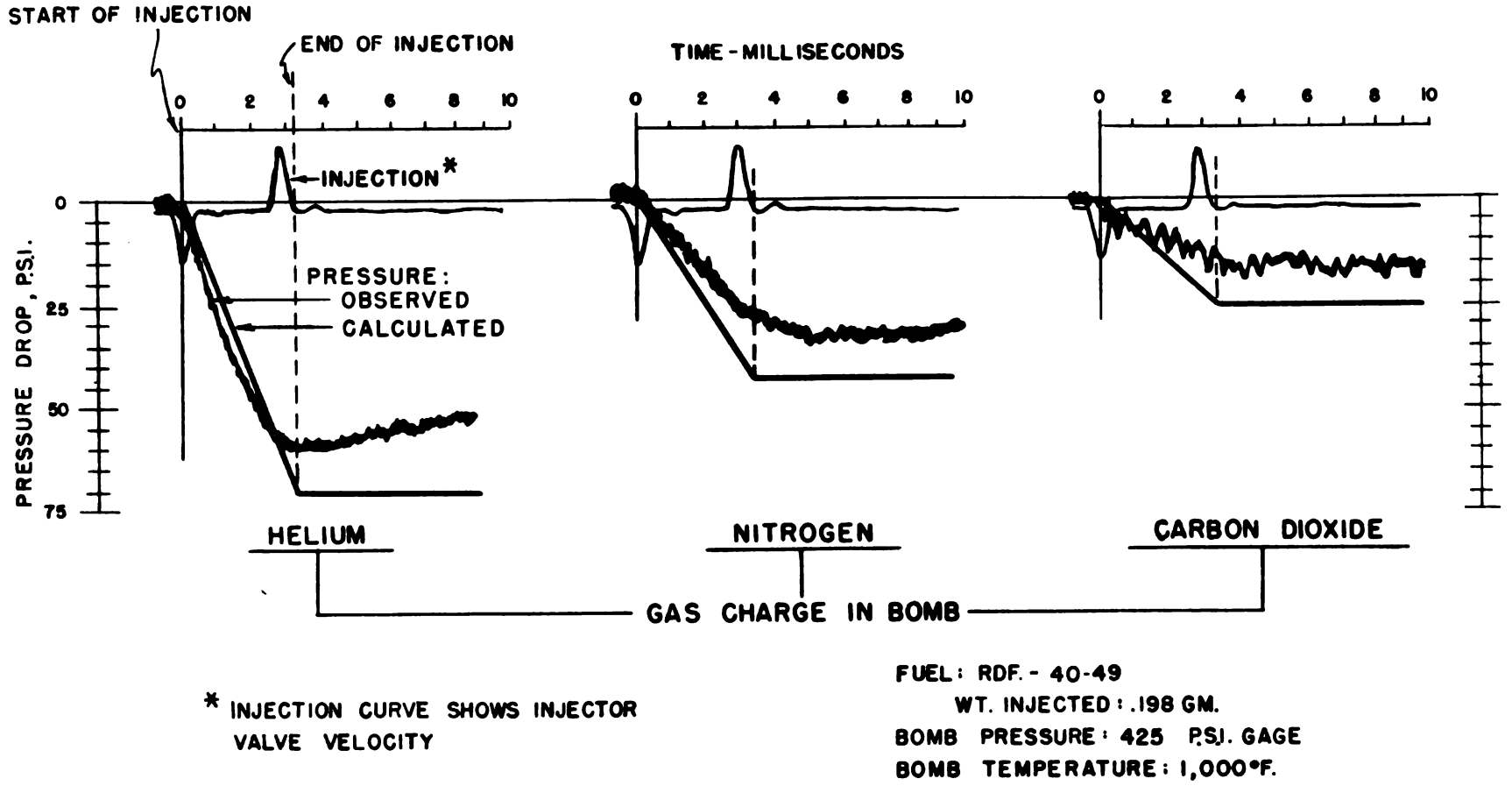

Figure 14. - Observed and calculated pressure records - fuel injected into inert gases (using constant-volume combustion bomb).

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Engine Studies

Only routine cetane-number and octane-number evaluations of fuels were made during the year in the engine laboratory. However, significant contributions to research preparations were made by installing a Diesel research unit, equipped with a d.c. dynamometer, to test combustion characteristics of fuels over a wide range of engine speed and load conditions. Instrumentation was devised to yield positive indication of the ignition delays encountered in engine combustion.

Results of investigations of the combustion characteristics of certain pure hydrocarbons were published.52/

Fuel Surveys

Three reports appeared during the fiscal year, giving the results of one survey of motor gasoline,53/ one survey of aviation and jet fuel,54/ and one survey of Diesel fuel.55/ Another motor-gasoline-survey report for the winter 1951-52 was prepared during the fiscal year and appeared in July 1952.56/ The motor-gasoline survey reports have been "streamlined," so they are smaller in volume than formerly but contain the same amount of data.

These surveys are conducted under a cooperative agreement between the United States Department of the Interior, Bureau of Mines, and the American Petroleum Institute. Under the agreement, samples of the fuels are analyzed in the laboratories of oil, chemical, and motor companies by standard procedures and the results submitted to the Bureau of Mines for compilation and publication. The reports are in demand by refiners of petroleum, chemical and motor manufacturers, and consumers who need information on the properties of motor gasoline, aviation fuels, and Diesel-fuel oils. For example, Technical Committee A on motor gasoline, of Committee D-2 of the American Society for Testing Materials utilizes the data from the motor-gasoline surveys to establish the octane number limits in its gasoline specification D439, and Technical Committee F of the same organization is employing the Diesel-fuel reports in preparing Diesel-fuel specifications.

Composition of Petroleum Asphalt

The study begun last year to evaluate petroleum asphalt by determining the amounts and types of its different hydrocarbon fractions was continued. A 600-gram sample of asphalt from Oregon Basin, Wyo., crude oil was separated into two crude fractions, pentane-insoluble asphaltenes (yield 21.9 percent) and pentane-soluble

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52/ Hurn, R. W., and Smith, H. M., Hydrocarbons in the Diesel Boiling Range: Ind. Eng. Chem., December 1951, vol. 43, pp. 2788-2793.

53/ Blade, O. C., National Motor-Gasoline Survey, Summer 1951: Bureau of Mines Rept. of Investigations 4854, 1952, 24 pp. Octane Ratings of U. S. Motor Fuel Drop from Record Levels: Oil and Gas Jour., Feb. 4, 1952, p. 76.

54/ Blade, O. C., National Annual Survey of Commercial Aviation Gasoline and Aviation Jet Fuel, October 1951 Production: Bureau of Mines Rept. of Investigations 4889, 1952, 13 pp.

55/ Blade, O. C., National Annual Diesel-Fuel Survey, 1951: Bureau of Mines Rept. of Investigations 4830, 1951, 12 pp. Annual Diesel-Fuel Survey, 1951: Oil and Gas Jour., Jan. 21, 1952, p. 98.

56/ Blade, O. C., National Motor-Gasoline Survey, Winter 1951-52: Bureau of Mines Rept. of Investigations 4901, 1952, 24 pp.

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petrolenes (yield 78.1 percent). The asphaltenes were fractionated further by extensive extraction with pentane (yield 10.9 percent) followed by extraction with ethyl ether (yield 9.8 percent). The petrolenes are being fractionated by extraction with n-butyl alcohol. The properties of these fractions and others to be prepared later will be determined.

Based upon previous work, an article was prepared[57] concerning variations in different lots of anhydrous crystalline alumina used as an adsorbent in constituent analyses of asphalt. Owing to these variations, the same lot of alumina adsorbent should be used in series of analyses to obtain comparable results.

THERMODYNAMICS OF PETROLEUM

The refining of petroleum and the manufacture of special products from petroleum have, in large measure, become scientifically controlled procedures. The days of trial-and-error and rule-of-thumb have now yielded to the slide rule and calculating machine. This progress has been possible because scientists have broken down crude petroleum into its constituent parts and determined the properties of the more important of the hundreds of different substances present in crude oil. The acquisition of knowledge concerning the thermodynamic properties of the individual constituents of petroleum has been one of the primary factors in this systematization of the science of petroleum.

To aid in the continuing advance of petroleum technology, the Bureau of Mines maintains a well-equipped thermodynamics laboratory at Bartlesville, Okla. This laboratory has completed many investigations of the fundamental properties of hydrocarbons and related substances that have given it an international reputation. In the past, most of the substances studied have been pure hydrocarbons (substances containing only carbon and hydrogen), but the indications are that in the future, because of the rapid growth of the petrochemical industry, increasing attention will be given to substances obtained by chemical treatment and modification of the ingredients of crude petroleum. The petrochemical industry that uses hydrocarbon substances as raw materials to manufacture a host of useful products, such as rubber, plastics, anti-freeze, detergents, and insecticides, is one of the fastest growing industries in the country and is destined to become one of the industrial giants. It is necessary for progress that the substances used in this phase of chemical industry be studied in detail and that their thermodynamic properties be measured.

The current program of the thermodynamics laboratory can be broken down into the four following areas of interest: (1) Study of the important thermodynamic properties of pure hydrocarbons. This is a long-range program aimed at clearing up the many unexplored corners of hydrocarbon technology. (2) Systematic study of the thermodynamic properties of sulfur compounds found in or derivable from petroleum. This work is done in cooperation with the American Petroleum Institute under its Research Project 48A and is designed to give information that will lead to improved methods of manufacture of useful sulfur compounds and elimination of harmful or obnoxious products from petroleum fuels. (3) A special project to determine some of the important properties of lead tetraethyl and related substances. Lead tetraethyl is a key substance in the preparation of premium gasoline fuels and strangely, it has resisted attempts to elucidate its properties. This work is supported in part by one of the major producers of this important compound. (4) A beginning has been made in studying halogen and oxygen-containing substances, and in time it is hoped to expand this work to provide service to the research worker in the petrochemical field.

57/ Hubbard, Rethel L., Stanfield, K. E., and Kommes, W. C., Anhydrous Alumina as Adsorbent in Constituent Analysis of Asphalt: Anal. Chem., vol. 24, No. 9, 1952, pp. 1490-1491.

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Investigations in the thermodynamics laboratory are conducted to obtain information that will make it possible to calculate the yields of chemical processes, the temperatures and pressures at which industrial processes can be operated, the temperatures at which certain compounds may be expected to decompose, and will permit efficient design of large-scale refinery equipment. These objectives necessitate: (1) Determining the heat capacity and other low-temperature properties of the substance of interest; (2) measuring heats of combustion and formation; (3) obtaining vapor heat capacity and heat of vaporization data; (4) studying vapor-liquid equilibria at high and low pressures; and (5) utilizing the experimental calorimetric results together with spectroscopic data to evaluate, by computational methods, properties of hydrocarbons, and other petrochemicals at temperatures and pressures that are inaccessible to laboratory measurement. Accomplishments in these five fields of investigation during 1952 are described in the following sections.

Low-Temperature Calorimetry

The ability of a given chemical substance to participate in chemical reactions is measured in part by a property that chemists and physicists have named entropy. This property may be measured by observing the ability of the compound to absorb heat at extremely low temperatures and on up the temperature scale to the region where industrial chemical reactions are conducted. The required low temperatures are obtained by using liquid hydrogen and liquid air. The necessary measurements are made with electrical heaters, thermometers, and measuring devices of the most refined type. Highly trained scientists are needed for effective use of this equipment.

The antiknock qualities of a gasoline have been shown to depend on the symmetry of the hydrocarbon components of the fuel. One of the most symmetrical molecules in the gasoline range is 2,2,3,3-tetramethylbutane. The low-temperature heat capacity of this substance has been determined, and a value of its entropy has been calculated. The results of this investigation are now available.58/ Other hydrocarbons studied by the same techniques are 2,3-dimethyl-2-butene, 1-heptene, 1-octene, 1-nonene, 1-decene, and 1-undecene. The results are being submitted to the American Petroleum Institute for distribution to research laboratories of the petroleum industry. Cycloheptane and cyclononane have been investigated for the first time. The first named of these two was only recently identified in crude petroleum. This illustrates that petroleum is still yielding secrets to investigators.

The program, sponsored and supported by American Petroleum Institute Research Project 48A, to obtain thermodynamic data for all sulfur compounds of importance in petroleum, made excellent progress during 1952. Complete studies were made on thiacyclopropane (ethylene sulfide),59/ ethanethiol (ethyl mercaptan),60/ 1-pentanethiol

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58/ Scott, D. W., Douslin, D. R., Gross, M. E., Oliver, G. D., and Huffman, H. M., 2,2,3,3-Tetramethylbutane: Heat Capacity, Heats of Transition, Fusion and Sublimation, Vapor Pressure, Entropy and Thermodynamic Function: Jour. Am. Chem. Soc., vol. 74, No. 4, Feb. 20, 1952, p. 883.

59/ Guthrie, G. B., Scott, D. W., Waddington, Guy, Thiacyclopropane (Ethylene-sulfide): Infrared Spectrum, Vapor Pressure, and Some Thermodynamic Properties: Jour. Am. Chem. Soc., vol. 74, No. 11, June 5, 1952, p. 2795.

60/ McCullough, J. P., Scott, D. W., Finke, H. L., Gross, M. E., Williamson, K. D., Pennington, R. E., Waddington, Guy, and Huffman, H. M., Ethanethiol (Ethyl Mercaptan): Thermodynamic Properties in the Solid, Liquid and Vapor States. Thermodynamic Functions to 1,000° K.: Jour. Am. Chem. Soc., vol. 74, No. 11, June 5, 1952, p. 2801.

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(amyl mercaptan),[61] and 3,4-dithiahexane (diethyldisulfide).[62] Other sulfur compounds on which low-temperature measurements have been completed are thiacyclopentane,[63] 2,3-benzothiophene,[63] 2-butane-thiol,[64] and thiacyclobutane.[64] The low-temperature properties of tetramethyllead also were determined. This study of a relatively simple molecule will help in understanding the properties of the more complex fuel additive tetraethyllead.

Vapor-Heat Capacity and Heat of Vaporization

The heat required to vaporize liquid hydrocarbons and that needed to raise the temperature of hydrocarbon vapors are two valuable properties of importance in chemical theory and in engineering practice. The experimental equipment for measuring these quantities has been improved during the past year through the construction of a vaporizing unit made entirely of glass and platinum. This construction permits study of substances that induce corrosion of ordinary metals. A new vapor calorimeter has been built that permits much more rapid measurement of vapor-heat capacities. Special valves of unique types have been devised for handling corrosive sulfur compounds. The new equipment has been used to study two sulfur compounds (thiacyclobutane[63] and 3-methylthiophene[64]) and water (manuscript in press). Water is one of the end products of fuel combustions of liquid fuels and enters importantly into calculations pertaining to the efficiency of engine operation. Heretofore, experimental techniques have not been available for carrying out heat-capacity measurements on water vapor.

Combustion Calorimetry

Possibly the most important thermodynamic property of a chemical compound is its heat of formation. There is no known way of calcuting this property. It can only be found by carrying out direct measurements in the laboratory of the amount of heat evolved when a weighed amount of the substance is completely burned under controlled conditions. Pioneering development in the Bureau of Mines Thermodynamics Laboratory has resulted in a rotating bomb capable of yielding values of the heat of formation of corrosive substances such as sulfur- and chlorine-containing compounds. This equipment is the first of its kind in the United States and will find a very wide field of application in the future. In the foreground of figure 15 may be seen the ruggedly constructed bomb with external gears for imparting two types of rotation. This unit, made of heavy stainless steel lined with platinum is about 6 inches long. In the background of the photograph is the polished metal container that houses the bomb when experiments are in progress. The International Union of Thermochemistry has asked this laboratory to prepare two chapters dealing with the application of this new development to the combustion of sulfur and chlorocompound combustions for a forthcoming book on Experimental Thermochemistry. These chapters are now in preparation. The new equipment has been used to obtain heat of formation values for 3-thiapentane,[65] 2-methyl-2-propanethiol,[65] and thiacyclopentane.[65] A manuscript

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61/ Finke, H. L., Scott, D. W., Gross, M. E., Waddington, Guy, and Huffman, H. M., The Entropy and Vapor Pressure of 1-Pentanethiol: Jour. Am. Chem. Soc., vol. 74, No. 11, June 5, 1952, p. 2804.

62/ Scott, D. W., Finke, H. L., McCullough, J. P., Gross, M. E., Pennington, R. W., and Waddington, Guy, 3,4-Dithiahexane; Heat Capacity, Heats of Fusion and Vaporization, Vapor Pressure, Entropy and Thermodynamic Function, Jour. Am. Chem. Soc., vol. 74, No. 10, May 20, 1952, p. 2478.

63/ American Petroleum Institute Research Project 48A, Annual Report 4: Oct. 1, 1951, p. 9.

64/ American Petroleum Institute Research Project 48A, Quarterly Report 10: Apr. 1, 1952, p. 9.

65/ American Petroleum Institute Research Project 48A, Quarterly Report 10: Apr. 1, 1952, table 5.

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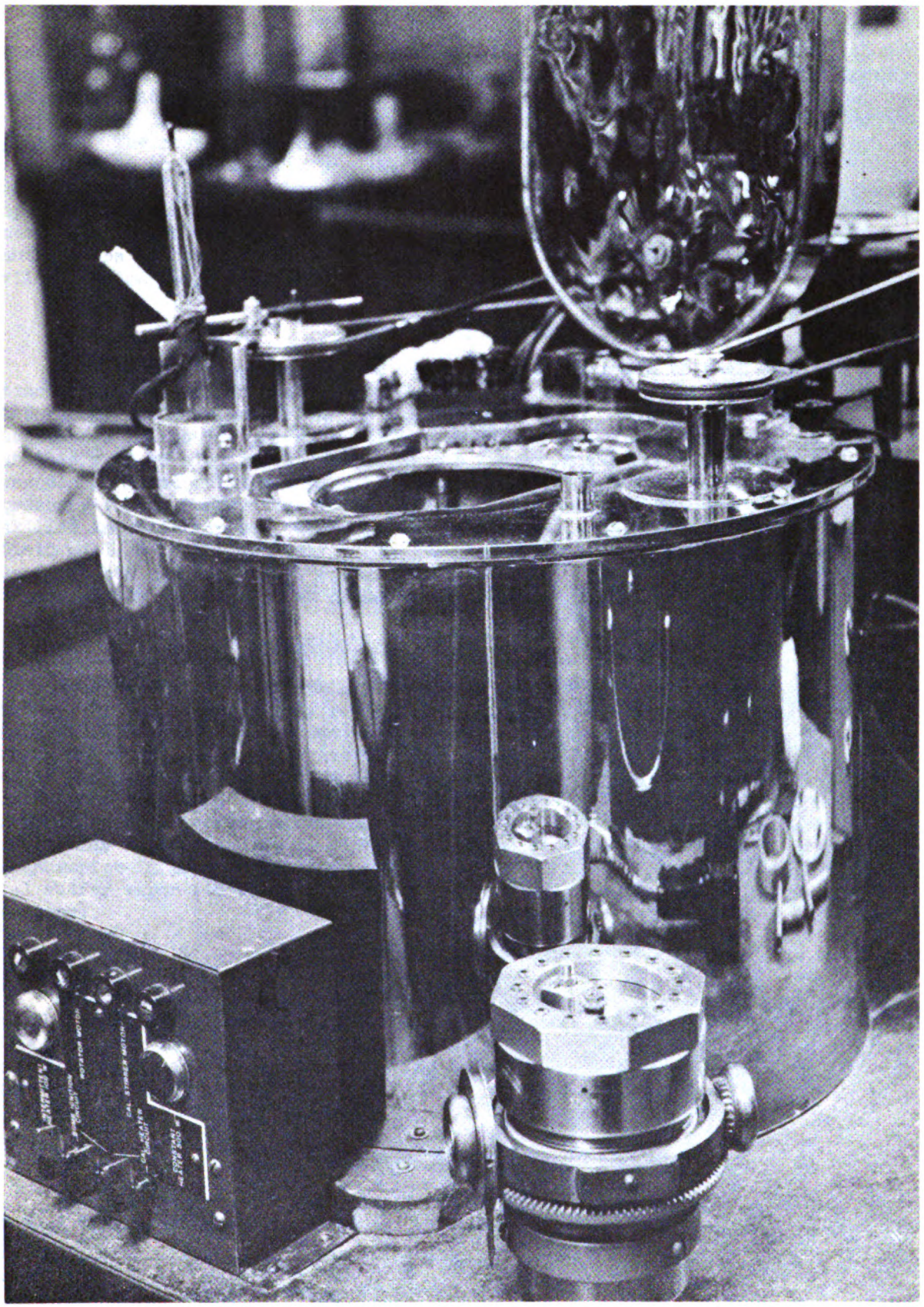

Figure 15. - Rotating bomb and its constant-temperature container used for studies of the heats of combustion of corrosive sulfur compounds.

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describing work on the last-named compound is now in press. Special combustion-bomb equipment has been designed and constructed for determining the heat of formation of tetraethyllead. This problem is one of peculiar difficulty because of the different varieties of lead oxides that normally are produced as a result of the combustion process. The results are of unusual interest and importance to the tetraethyllead industry. A second special project that has been begun aims at determining the heat of formation of fluorocarbons, which are of interest in connection with plastics, special lubricants, and a number of military applications. Preliminary steps have been taken to activate this work. During the year two of the foremost European authorities on combustion bomb calorimetry have made extended visits to the Bartlesville Station to obtain a knowledge of the techniques being used.

Vapor-Liquid Equilibria

Many industrial processes are carried out at moderate to high pressures as distinct from ordinary or atmospheric pressure. For several years the Thermodynamics Laboratory has been measuring the vapor pressures of liquid hydrocarbons and related substances in the low-pressure range, but it has been recognized that an extension of this work to high pressures was of the utmost importance. In 1952 a laboratory was designed and built and partly equipped for high-pressure investigations of the pressure-volume-temperature relationships of hydrocarbons and petrochemicals. A skilled investigator has been engaged to lead this work, and development in this field will be pushed actively. The low-pressure (vapor-pressure) equipment has been used to obtain data for the compounds 2,3-dimethyl-2-butene, cycloheptane, cyclooctane, furan (manuscript in press) 2-butanethiol, and 1-butanethiol.

Statistical Mechanical Calculations

Results of the experimental investigations described in the foregoing sections are useful when taken singly but achieve maximum utility when they are suitably correlated. Chemical theory permits the application of computational methods, which bring together all the experimental data into a set of useful tables readily applicable by industrial research workers and at the same time extending the range of usefulness of the laboratory investigations to much higher temperatures than can be reached by direct experimentation. Use of these methods has permitted compilation of tabular data extending to high temperatures for thiacyclobutane, thiacyclopentane (manuscript in press), 3,4-dithiahexane,[62] 2,2,3,3-tetramethylbutane,[58] and elemental sulfur vapor (to be presented orally at a national American Chemical Society meeting).

TRANSPORTATION OF NATURAL GAS

Research in the field of natural-gas transportation and processing is conducted at the Amarillo Helium Plant, Amarillo, Tex., in cooperation with the American Gas Association. In 1952, this research included: (1) The problem of removing excess nitrogen from natural gas; (2) development of a continuous automatic dew-point recorder to improve natural gas plant and pipeline operation; and (3) a study of the flow of natural gas in pipelines.

Removal of Excess Nitrogen from Natural Gas

No experimental work was done on this problem in 1952, but a report[66] was issued discussing the suitability of six possible methods of removing excess nitrogen

66/ Mullins, P. V., and Wilson, R. W., Prospective Methods and Estimated Costs for Removing Excess Nitrogen from Natural Gas: American Gas Association PAR Report, April 1952, 15 pp.

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from natural gas. The methods are: (1) Chemical absorption; (2) hydrate formation; (3) physical absorption; (4) adsorption; (5) diffusion; and (6) low-temperature processing. Only two methods - adsorption and low-temperature processing - appear to be promising. The probable cost of removing excess nitrogen, based on meager data that were available, was estimated to be 2-1/2 to 3 cents per 1,000 cubic feet of natural gas processed. This indicates that there is little or no prospect for economic gain because of increased pipeline deliverability resulting from removal of excess nitrogen at the present time. However, additional economic benefits might result from coincidental dehydration of the gas, increased LPG (liquefied petroleum gas) recovery and, in some instances, improved marketability. These factors can be appraised only by individual specific analyses of the circumstances in each case.

Dew-Point Recorder for Natural Gas

The continuous automatic dew-point recorder developed by the Bureau of Mines in cooperation with the American Gas Association is being manufactured and sold by a private concern, and it is being used by many natural-gas-processing plants and pipelines.

The instrument does an excellent job of measuring and recording the water-vapor contents of gases that have been treated in dehydration plants utilizing activated alumina or diethylene glycol. It has not been entirely successful when used to determine the water-vapor content of gas that has been treated in acid-gas removal plants utilizing one of the amines alone or in conjunction with diethylene glycol.

The problem is to find some substance, probably acidic in nature, that will react with amine vapors and produce a reaction product that will not carry over in vapor form and affect the hygrometer element. Oxalic, benzoic, and oleic acids have been moderately successful, but there are still some difficulties to be solved before the instrument can be used successfully when amine vapors are present in the gas stream to be tested.

Flow of Natural Gas in Pipelines

The objective of this research is to develop accurate gas-flow formulas to use in designing new transmission lines and determining the efficiency of existing lines.

The first part of the study - a review of literature and current use - has been completed; and considerable progress has been made in the second part - experimentation with comparatively short experimental lines. Many flow tests have been made in the Bureau's Cliffside gas field near Amarillo, Tex., and in the Goleta, Calif., gas-storage field of Pacific Lighting Gas Supply Co. These tests utilize seven experimental pipelines, one of which is of seamless-steel pipe that was bored and honed at the Naval Gun Factory, Washington, D. C., to mirror finish and uniform internal diameter.

Although the results obtained to date have been informative, they have not been conclusive, and additional flow tests will be made in the near future. It is believed that the occurrence of condensate and dust in the lines during some of the tests has affected the results, and efforts will be made to obtain uniformly dry gas for future tests and to filter the gas more effectively.

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